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Damage to Limestone Exposed to High Temperatures - A Review

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ABSTRACT

Previous studies showed that fire incidents cause a considerable deterioration of limestone samples' engineering and physical properties. Various laboratory tests were used in previous studies to investigate the properties of limestone. These tests included destructive and non-destructive tests like the hammer test, ultrasonic pulse velocity test, water-capillary rise test, and water transfer properties test, as well as destructive tests like the unconfined compression test and Brazilian tensile test. The stones of buildings exposed to fire are occasionally assessed on the site. This study analysed the physical and mechanical changes that occurred to the limestone samples when subjected to high temperatures, the damage mechanism, and laboratory or field damage assessment. This study also includes a review of the most significant studies that looked at how alternative cooling techniques—rapid water cooling or gradual air cooling—affect stone samples subjected to high temperatures and compared the behaviour of the samples in each scenario.

1. Introduction

Humans have used wood to build buildings since ancient times. However, with time, many available and alternative materials were used, such as limestone, sandstone, brick, and concrete. Regarding limestone, it has been used in ancient monuments and wonders of the world, such as the massive construction of the Sphinx and the Pyramids of Giza in Egypt [1], even in the case of modern monuments such as the Arc de Triomphe in Paris and the Lincoln Memorial in Washington, USA [2]. One kind of stone that was frequently utilized in the field of civil engineering was limestone. Thus, it is imperative to comprehend its behavior and resilience to various circumstances, including daily and seasonal fluctuations in temperature and humidity [3] and the regular occurrence of natural disasters like fires[4-6]. In this regard, it is crucial to understand how high temperatures or fires affect building materials such as limestone. Determining the process by which fire causes damage is also essential. Examining the impact of high elevated temperatures also aids in making an informed choice about the necessary actions for managing fire-prone structures. The choice is crucial in this instance, particularly when handling archeological sites or old historical structures. Limestone has been a fundamental building element for structures for thousands of years. Given that this building is often constructed of stone, the limestone represents a significant portion of the cultural legacy. .In northern Iraq, limestone has been widely used for millennia in several historical structures and monuments[7-8]. Mosul is significant both geographically and historically. Regretfully, many of this city's structures, particularly those in Mosul's ancient city, which is situated on the western banks of the Tigris River, have suffered significant damage recently. Indeed, fire was the primary source of a large amount of this damage. Many structures in Mosul were destroyed during the 2017 liberation operations of Nineveh Governorate; the majority of this devastation was caused by the damage, particularly fire damage, that the ancient city of Mosul sustained at that time. Heat damage is considered a major concern in engineering projects, such as tunneling, nuclear transactions, thermal energy modeling, and other projects [9]. Events involving fire are severe and essential to building security. In this regard, examining the mechanical and physical properties of natural stones and the chemical changes caused by exposure to high temperatures is essential. The kind of fire suppression chemical employed during the extinguishing procedure and the fire smoke can potentially cause damage to building structures. In this regard, the building must remain stable for a set period to evacuate people during a fire and by public safety rules. Additionally, the safety of structures exposed to fire must be guaranteed when performing maintenance and repair.

Stones' mechanical and physical properties must be understood when exposed to high temperatures. Temperature is one of the main variables affecting the microstructure of rocks. For example, significant temperature fluctuations change the engineering behavior of stones by causing pre-existing cracks to enlarge and new ones to form.

Investigating how stones behave when exposed to a range of temperatures is crucial. Numerous studies have looked into this topic from different perspectives. Some studies examined physical characteristics including density, color, appearance, and hardness [10-16]. While other studies focused on locking at the mechanical and engineering properties of stones, such as compressive and tensile strength, modulus of elasticity, Poisson’s ratio, and ultrasonic pulse velocity[17-25]. Several additional researchers have examined how exposure to high temperatures affects the chemical and mineralogical composition of stones[9][19][26-29]. Many studies are conducted in laboratories or through experiments. However, it is still possible to conduct a field study to determine the extent of damage that high temperatures cause to building stones..[30-33].

The preceding lines highlight the significance of earlier studies in figuring out how limestone behaves at high temperatures and the need for more future research in this field. The purpose of the current review study can be summarized in the following points:

- Determining the mechanism by which stone samples are damaged after exposure to high temperatures.
- Review the most notable findings from earlier studies and outline the key tests that may be used to assess limestone's engineering behaviour following exposure to high temperatures.
- Determining the types of laboratories and field testing and the classification based on destructive and non-destructive test types are other important aspects of this study.
- Looking at the most effective ways to cool stone samples after exposure to high temperatures and how these various cooling methods affect the engineering behaviour of stones.

2. Mechanism of rock damage due to heating

Physical and chemical processes accompanying stones when exposed to high heat are the development or expansion of cracks, the breaking of chemical bonds, and the transition of minerals from one phase to another, which are associated with drying processes. In addition, the stones contain different minerals that have different coefficients of thermal expansion, and this will lead to the occurrence of internal stresses due to the differential thermal expansion of the different minerals composing the stones, which may increase the tensile strength of the stones and thus cause damage to those stones. In addition, the mechanism of stone deterioration due to heat is that the difference in the coefficient of thermal expansion of the minerals that make up the stones causes damage during exposure to repeated temperatures, which causes fatigue damage. These changes affect the mechanical properties of stones, including compressive/tensile strength, permeability, stone deformation, and heat transfer conductivity, Figure (1). The heating processes will also alter the stones' physical properties: color change, increased porosity, and water loss. Again, exposing the stones to high temperatures changes the mineral lattice due to the loss of crystalline water.

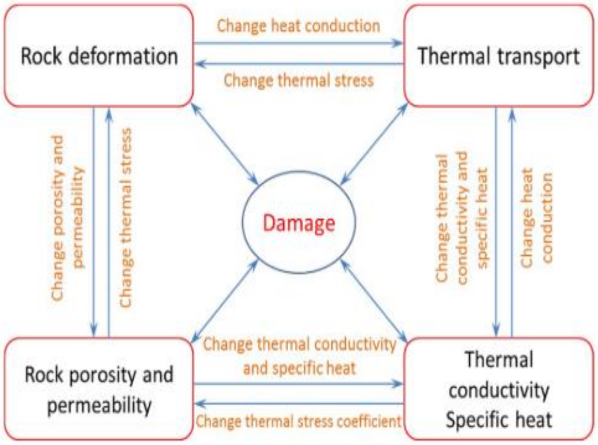

Figure 1. Damage mechanism of stones when exposed to high temperatures [34]

3. Assessment of the stone damage in recent fires

Structures are typically severely damaged by fires, especially historical ones. It is, therefore, essential to ascertain how the fire affected the structural integrity of the building and the stone materials used in its construction, as well as any aesthetic modifications like a color alteration. One of the ancient structures that was subjected to a high-intensity fire was Windsor Castle in the United Kingdom, On the first level of Chester Tower, which is situated in the northeastern part of the structure, there was a private chapel where the fire started. Smoke and fire caused severe damage to the stones [35].

Guibaud et al., 2023 [31] were interested in examining the 2019 Notre-Dame de Paris fire in another research article. Two limestone sources were subjected to preliminary laboratory testing before the reconstruction. First, limestone samples were analyzed from the Saint-Maximin quarry in the northern region of France. Second, limestone samples from the vault's collapsed roof were analyzed; the samples were subjected to a temperature range of 25 to 700°C. Several tests were performed, such as differential scanning calorimetry (DCS) and thermogravimetric analysis (TGA) for the limestone samples heated to temperatures higher than 600°C. The approach of Guibaud et al., 2023 [31] allowed the assessment of the rate of decomposition of portlandite and focused on the color gradation of the burnt stone. The results indicated that the limestone is initially pink or red when the temperature ranges between 250 and 300 °C. When it reaches 400 to 500 °C, its color turns gray; When it begins to decarbonize, it turns white (higher temperatures range between 600 and 700°C) [31] .Furthermore, the Al-Tahira Church in Mosul's old city, which was recently exposed to fire during the city's liberation in 2017, raised the interest of the researchers [33]. This church's columns were subjected to field testing, including ultrasonic pulse velocity measurements and Schmidt hammer tests. The data analysis showed many fractures formed in interior and external stone columns.

4. Assessment of stone damage due to heating

Researchers typically resort to laboratory experiments or field measurements to examine the effects of heat exposure on stones. These tests may also be non-destructive or destructive. The following paragraphs will review the most important studies concerned with this topic.

4.1 Damage assessment in laboratory

Temperature impacts the strength and engineering behavior of stone materials. When exposed to high temperatures, the stone's interior structure is affected, new fractures arise, and pre-existing fissures enlarge. Simultaneously, stones experience a range of physical alterations and mineral changes in texture. Researchers typically employ a set of laboratory experiments to assess the damage to fired stones. Destructive testing and non-destructive tests are the two types of these tests.

4.1.1 Non-destructive tests

Using the stone samples for additional testing is one advantage of the non-destructive tests. This is because the stone sample is not destroyed throughout these tests. Apart from preventing adverse effects, reducing equipment expenses, and ensuring maximum safety, these tests are also easily practicable in the field [36]. Non-destructive testing is widely used to detect internal defects in stone samples by measuring mechanical properties without affecting the physical stone properties both in situ and in the laboratory [37]. The capillary water absorption test (Imbibition test), the Schmidt hammer test, and the ultrasonic pulse velocity test are examples of non-destructive tests. Other types of non-destructive tests include the Archimedes principle test, commonly known as the water saturation test method, usually used to measure the density, specific gravity, and total porosity of the stone samples [38]. Examining the outside appearance and color of stone samples before and after alteration is one of the other non-destructive tests. The following paragraphs demonstrate the most common non-destructive tests.

4.1.1.1 Appearance

Appearance is a physical property of stone samples. Appearance check is classified as a non-destructive test. This test can be used to investigate the effect of temperature on the outer surfaces of stone samples. A regular digital camera can take pictures before and after the test and compare the two cases. However, special image capture devices analyze the surface image of stones according to three main variables (a, b, and L). As shown in Figure (2), the coordinate (a) refers to the x-axis in which negative values are green and positive values are red. The coordinates (b), which refers to the y-axis and blue/yellow variation, negative values represent blue, and positive values represent yellow [39-40].

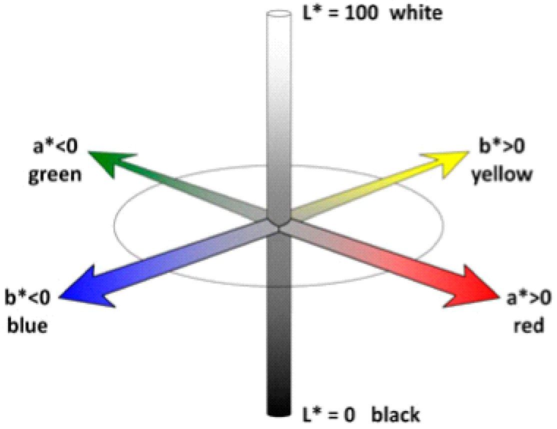

Figure 2. Colour coordinates in colorimeter measurement. After [39]

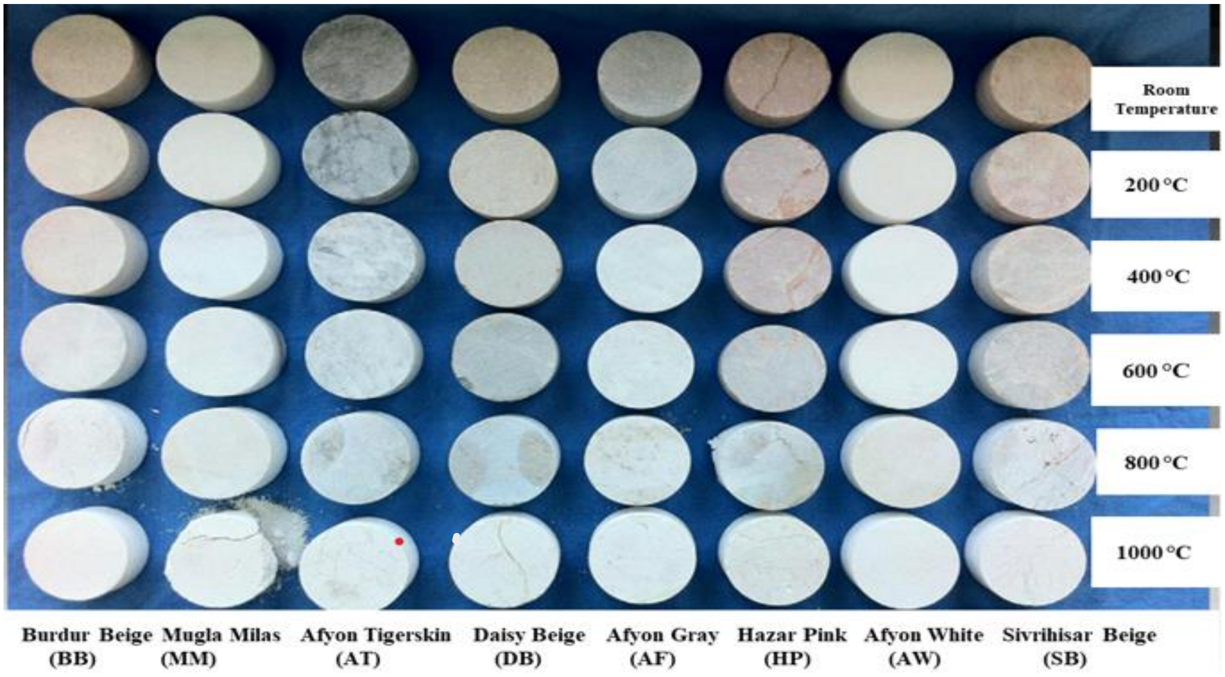

Figure 3. Effect of high temperature on limestone [42]

The experimental work of [41] Studied limestone's colour and external appearance at high temperatures, especially when the temperature reaches 1000 °C. The results indicated that the rock samples are exposed to water evaporation when temperatures rise from 150 to 400 °C. This indicates that the samples have invisible cracks. When the temperature rises from 400 to 600 °C, the color of the samples changes to light white, as some large, wide cracks gradually increase. When the temperature rises from 600 to 1000 °C, the color gradually changes from light gray to pure white, and the cracks increase significantly. The cracks generally adhere and form open conjugate cracks at the final heating temperature. On the other hand, [42] They were Adopted to study the colour characteristics of limestone and Turkish marble. The stone samples were exposed to high temperatures from 200 to 1000 °C. The results showed that the colour property is greatly affected at 800 °C, while the samples become white at 1000 °C, as shown in Figure (3).

4.1.1.2 Ultrasonic pulse velocity

Ultrasonic pulse velocity test has been a non-destructive technique in civil and geophysical engineering applications for many years. Ultrasound pulse velocity tests present many advantages for evaluating the strength of building materials, including concrete and stones, in addition to estimating the physical properties and detecting the presence of cracks in these materials [43]. According to (Bodare, 2017) [44], ultrasound may be defined as piezoelectric devices with a transmitter and a receiver. The transmitter sends a wave through the sample to the receiver, which is located on the other side. A receiver and transmitter transducers on the stone sample's opposed and parallel sides are used to achieve the ultrasound measurement. The sample length, which indicates the distance between the sending and receiving signals, calculates the time it takes for a sound wave to travel. The ratio of the ultrasonic wave's arrival time to its travel distance, or the length of the sample, is the physical definition of the ultrasonic pulse velocity test.

The effect of heat damage on the physical characteristics of carbonate stones, such as limestone and marble, was examined. [10]. The stone samples in this investigation were subjected to temperatures between 100 and 1500 °C. In that order, each temperature level's ultrasonic pulse velocity was measured following heating time cycles of 12, 24, 48, 96, and 144 hours. The findings showed that the sample groups' ultrasonic pulse velocities were lower following heat treatment than the initial values. In the study of (Andriani and Germinario, 2014) [45], the effect of thermal damage on carbonate stones was investigated at temperatures ranging from 100-700 °C. The ultrasonic pulse velocity was measured for each temperature level, and the results indicated that when the temperature increased, there was an apparent decrease in the measured velocity.

A study of (Zhang et al., 2015) [46], was also focused on studying the effect of high temperatures on the microstructure and the ultrasonic pulse velocity propagation in limestone over a wide range of high temperatures (25 to 900 °C. This study divided the tests into several stages according to temperature level. The results showed that when the temperature changed from 25 to 300 °C in the first stage, there was a slight increase in the sound velocity at 100 °C. It gradually decreased due to the evaporation of water inside the sample, which led to a change in the sound velocity.

The ultrasonic pulse velocity showed a tendency inversely related to the temperature change in the second stage (300-600 °C), where it fell dramatically with temperature. Because all the water was lost, the ultrasonic pulse velocity dropped from 5.482 km/s at 300°C to 2.360 km/s at 600°C. As for the third stage, 600-900 °C ultrasonic pulse velocity, very little variation was found in the ultrasonic pulse velocity values for the examined samples. Moreover, the non-destructive testing was lately carried out on limestone samples from Azerbaijan [2]The stone samples were subjected to a temperature range of 100–800°C. The findings indicated that, at 100 and 200°C, there is no discernible change in the ultrasonic pulse velocity; nevertheless, at 400°C, the ultrasonic pulse velocity dramatically reduces, and at 600 and 800°C, the decline in these velocities is more severe.

4.1.1.3 Imbibition test

When limestone samples are exposed to high temperatures, studying the water transfer properties is very important. Water transport properties can be expressed through laboratory tests, such as free or forced water absorption, water retention, and water capillary rise tests (Imbibition tests). Identifying water transmission properties is an important characteristic in diagnosing the ability of stone samples to retain water, which is directly related to the texture and internal structure of stone samples [47].

In general, capillary action—in which water height within small-diameter pores is correlated with the capillary force generated—allows porous stone to absorb water in contact. The perfect wetting fluid is polar water, which may rise smoothly through the capillary pores of tested stones due to its favorable wetting angle. The cylindrical or cubic-shaped samples are typically used for the water capillary rise test. To keep the stone sample in direct touch with the water, it is placed in a basin with a wet towel and a certain amount of water. To ensure that the water level inside the basin stays consistent during the test period, the water's height is monitored throughout time [38, 48-49]. A typical result analysis of the water capillary rise test is the lines presented in Figure (4).

Two parameters are usually obtained: (Capillary front height coefficient - H and Water uptake coefficient - W), which represent the slope of the two lines [38].

$$h = H_{capillary} \times \sqrt{t} \qquad (1)$$

$$w/S = W_{Capillary} \times \sqrt{t} \qquad (2)$$

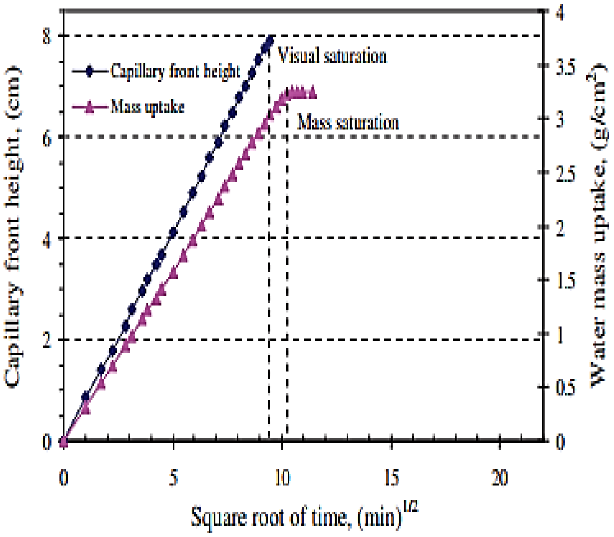

Figure 4. Typical curve from the water capillary rise test [38]

The goal of the research work of Ozguven and Ozcelik (2014) [11], was to determine if the capillary properties of various natural limestone samples impacted the absorption coefficient. Four natural limestone were included in this study: (BB: "Burdur Beige, it is a Sparitic limestone. Moderate crystalline calcite and a small amount of recrystallized thinney calcite veins and opaque minerals are present", DB: "Daisy Beige, it is a Biosparitic limestone. Moderately crystalline calcite and small amount of opaque minerals are present",HP: :"Hazar Pink, it is a Sparitic limestone. Bioclast, calcite and abundantly fossils are present", and SB: "Sivrihisar Beige, it is a Sparitic limestone. Moderate crystalline calcite and a small amount of recrystallized thinney calcite veins and opaque minerals are present") The water absorption coefficient by capillarity (WACC) was determined in this investigation.

The results demonstrated no appreciable change in the limestone's ability to absorb water through capillaries up to 200 °C. This can be attributed to the fact that the capillary cracks and/or capillary pores are not changed or affected within this limited temperature range. Nevertheless, at higher temperatures, an increase in the rate of capillary water absorption was observed, Figure (5).

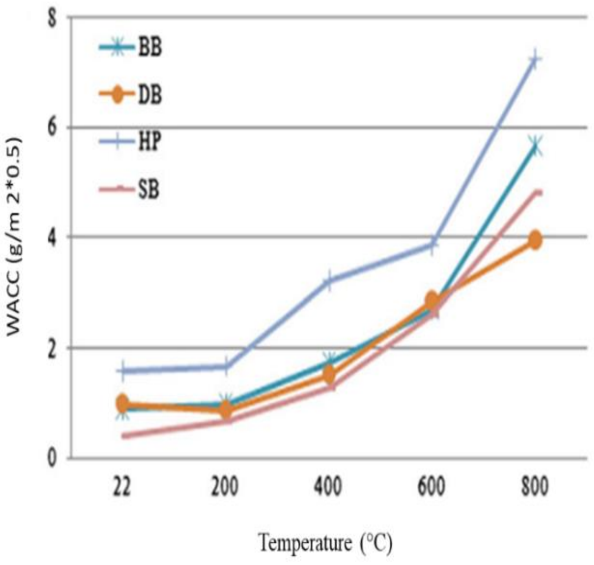

Figure 5. Effect of temperatures on the coefficient of water height by capillary action [11]

It should be mentioned that researchers have not frequently used the water capillary rise feature to look into the damage caused to stone samples after exposure to high temperatures. Thus, experiments are advised for this analysis to see how high temperatures affect the stone samples' water capillary rise property.

4.1.1.4 Water absorption test

In geotechnical engineering, measuring the water absorption of stone samples n purposes. The stone water absorption property is the ratio of water absorbed by the stone sample to the weight of the dry sample. It is important to note that this test has two possible formats: the free water absorption test and the forced water absorption test.

In the first test, the weights of the stone samples are measured after drying for 24 hours. The samples are then immersed in distilled water at room temperature for 24 hours under atmospheric pressure. In the forced water absorption test, air is drawn from within the pores of the dry stone samples under pressure. Here, all the open pores will be filled with water after being immersed in water (i.e. there is no air trapping in the pores). This method of test is based on Archimedes' principle for floating and submerged bodies, or what is called the water saturation method [38].

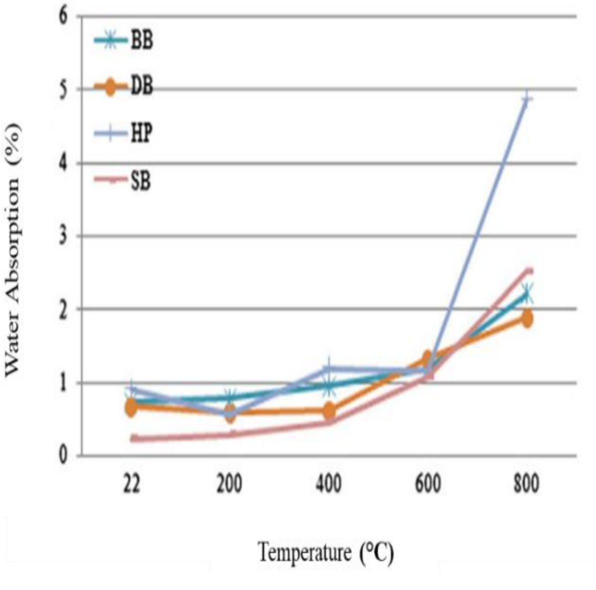

Figure 6. Effect of high temperatures on free water absorption test, [11]. Abbreviations (BB, DB, HP, SB) are the same as in Figure (5)

The goal of the study carried out by (Ozguven and Ozcelik, 2014) [11] was to determine how different limestone samples absorbed free water at temperatures as high as around 1000 ^{C}. As can be seen in Figure (6), the results showed that water absorption immediately increased with temperature.

4.1.2 Destructive tests

In geotechnical engineering, destructive testing is frequently utilized to ascertain the mechanical characteristics of stone samples. Measuring the strength of stone samples and other mechanical parameters, such as Poisson's ratio and modulus of elasticity, are additional mechanical properties that can be gathered from these tests. The stone samples are usually subjected to stress in these tests, which eventually causes the material to become warped or damaged after the test, making it unusable for further testing. The strength of stone samples is examined through the evaluation of destructive tests, such as uniaxial compressive strength, triaxial compression test, and different direct and indirect tensile strength tests: the Brazilian tensile test, point loading test, and bending test [50].

4.1.2.1 Unconfined compression test

Unconfined compressive strength is crucial for categorizing stone samples and architectural design. Furthermore, these mechanical characteristics are required to assess their appropriateness for different building uses. In this test, the stone sample under examination typically has a cylindrical shape, measuring "54 mm in diameter and having a length-to-diameter ratio of (2-3) [51]. This test is performed by subjecting the stone sample to a gradual axial load until the failure. During the test, vertical and/or horizontal deformations are monitored, and stress-strain curves are drawn, from which the modulus of elasticity (Young's modulus) and Poisson's ratio are also determined [52].

According to the experimental investigation conducted by (Mao et al., 2009) [21], limestone's mechanical characteristics are significantly affected by high temperatures between 25 and 800 °C, Figure (7). According to the findings, the stress and strain of the limestone samples only exhibit brittle deformation at ambient temperatures up to 400°C, Figure (8). At 600 °C, the stone samples show plastic deformation. This study also calculated the elastic modulus values for limestone samples. The results showed that the elastic modulus values decreased from room temperature to 200°C. While there is a slight change in the modulus values from 200 to 600°C, it decreases rapidly when the temperature exceeds 600°C, showing a decrease of 80% from 600°C to 800°C.

The experimental work done by (Brotóns et al., 2013) [53], showed that the high-temperature treatment had a noticeable impact on the mechanical characteristics (compressive strength, modulus of elasticity, and Poisson's ratio) of the Spanish San Julian limestone. The stone samples were subjected to temperatures ranging from 105 to 600 °C in this investigation. Different laboratory settings were used to cool the samples (both air and water). Destructive tests (uniaxial compressive strength) were performed on the samples. The uniaxial compressive strength of the air-cooled and water-cooled samples decreased by 35% and 50%, respectively, when the samples were heated to 600°C, as shown in Figure (7). In the case of the water-cooled and air-cooled samples, Young's modulus was reduced by 78% and 75%, Figure (8). The Poisson's ratio likewise drops with rising temperature in samples cooled by air and water by up to 44% and 68%, respectively.

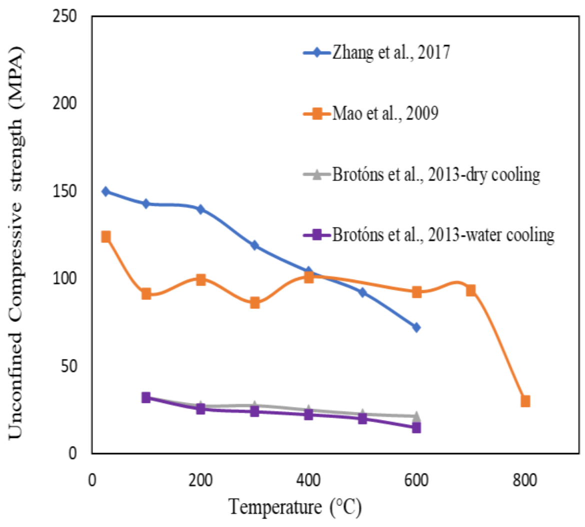

Figure 7. Effect of temperatures on compressive strength of limestone samples, the set of results of previous studies

Furthermore, a study of (Zhang et al., 2017) [54] Look at the engineering behavior of limestone when exposed to a restricted range of high temperatures (25 – 600 °C). This investigation performed a uniaxial compressive strength test and examined the parameters (modulus of elasticity and compressive strength). The findings showed that the stone samples' strength to failure reduced with increasing heating temperature (Figure 7). The same result was obtained for the modulus of elasticity (Figure 8).

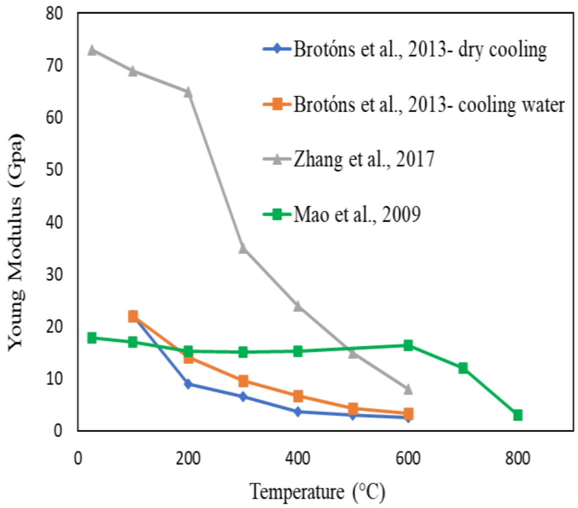

Figure 8. The results of previous studies show the effect of temperatures on the young modulus of limestone samples.

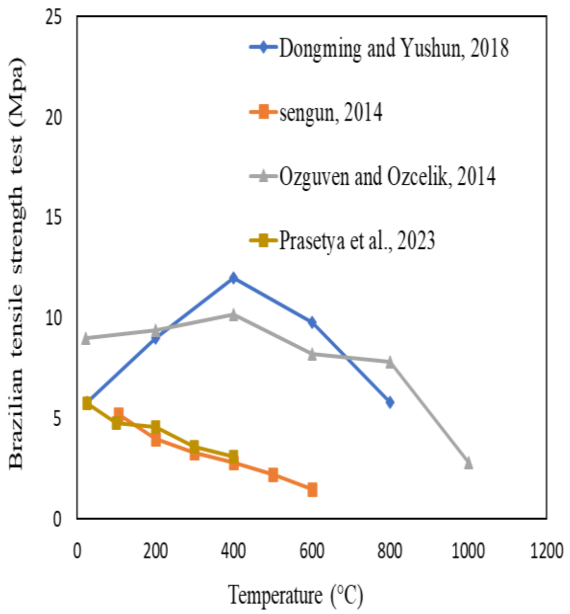

Figure 9. Effect of high temperatures on Brazilian tensile strength of limestone samples, the set results of previous studies

4.1.2.2 Brazilian tensile strength test

The Brazilian tensile strength is an important mechanical property for the strength classification of stone samples. In addition, this test is one of the most common indirect tests to measure the tensile strength of stone samples. The stone sample used in this test has a cylindrical form, too. A force delivered throughout the whole thickness of the disc is applied to a rock sample with a thickness of up to 0.5 in diameter, and the load is maintained until failure. A rock sample often divides along the vertical diagonal plane when it fails. The optimum fracture begins in the center and moves vertically in the direction of the loading points. [52]. In order to evaluate the Brazilian tensile strength, the researchers (Ozguven & Ozcelik, 2014), [11] was heated stone samples to 200–1000 °C. The findings demonstrated that natural stones' Brazilian tensile strength falls when the temperature rises. In these stone samples, a notable reduction in tensile strength was noted at 800 °C, Figure (9). In the same context, (Sengun, 2014)[55] was interested in investigating the Brazilian tensile strength by exposing the stone samples to temperatures ranging from 200-600 °C, Figure (9). It is noted that high temperatures of 600 °C cause a decrease in the Brazilian tensile strength of the stone samples by 75%. The research results of the experimental investigation carried out by (Prasetya et al., 2023) [56], Figure (9) shows the impact of temperature, which ranges from 25 to 400 °C, on the Brazilian tensile strength of the limestone samples. According to data analysis, at temperatures between 25 and 400 °C, the Brazilian tensile strength value decreased by 54.23%, and the Kic value—an equation that can be used to determine both the fracture toughness value and the value of the stress intensity factor—decreased by 54.22%.

In another study, (Dongming & Yushun, 2018) were interested in investigating the Brazilian tensile strength of limestone by exposing the samples to temperatures ranging from 25-800 °C, [20]. The results are shown in Figure (9). The results indicate that the Brazilian tensile strength increases with increasing temperature in the range of 400 °C, and later the tensile strength decreases with temperature increases from 400-800 °C. This indicates that the tensile strength of limestone is weak at 400 °C, but the tensile strength at 800 °C is still higher than the tensile 73.14 GPa at room temperature and decreases significantly from 100°C to 200°C. °C, followed by a relatively slow decrease from 200 °C to 600 °C, and more slowly at temperatures beyond 600 °C. The researchers attribute these abnormal findings to the fact that the change in the pre-existing pores and micro-cracks caused by the expansion of minerals with temperature results in a change in the tensile strength: an initial increase in the tensile strength then decreasing with more exposure to temperature [57].

4.2 Damage assessment in the field

Building fires may inflict substantial damage, as several incidents have demonstrated. For this reason, it's critical to determine how the fire will impact the building's structure and the materials used in its construction, particularly stone.

A decrease in strength, a change in appearance (color alteration), and other adverse impacts are a few examples of these effects. A review of previous studies in investigating the role of high temperatures and evaluating the range of stone deterioration materials through laboratory works and/or experimental studies has been referred to in the previous paragraphs. It is worth noting that the evaluation of stone materials can also be carried out in the field. Below is a list of some field studies through which damage is assessed to stone materials exposed to high temperatures or fire.

In January 2017, a fire occurred in the Byzantine monastery, another instance of a fire. The majority of the monastery cells were destroyed as a result of this fire [30]. Following the monastery's fire exposure, laboratory testing was carried out on the stone samples removed from the site. Optical microscopy, the Schmidt hammer test, and infrared thermal imaging were among these tests. The findings demonstrated that the influence of fire on the stone ingredients gives the limestone its tiny pink appearance. The calcite concentration was also found to have decreased according to thermal detecting and X-ray diffraction tests. Once more, the fire increased the stone samples' porosity, decreased their density, and increased their capacity to absorb water. Regarding non-destructive testing, the study's findings demonstrated that the fire's damage caused a definite decline in limestone's performance, as seen by the stone samples' significant reductions in surface hardness.

In another case of fire, the Church of Notre Dame was exposed to a fire in 2019 [31]Stone samples were taken from one of the basements of the northern wing, and some laboratory tests were conducted (colorimetric examination, SEM examination, thermogravimetric analysis (TGA), and differential scanning calorimetry (DCS)). The results showed that the temperature estimated by colorimetry (about 250 - 300 °C) and the presence of fine cracks in the hot areas is estimated at about 600 °C.

5. Stone samples exposure to high heating by direct flame

Examining how high temperatures affect stone construction materials in two different situations is important. In the first, there are direct flames (flame condition), and in the second, there is exposure to the elevated temperature by fire (oven condition). Comparing the variations in these materials' behaviors is also crucial. The investigation carried out by (Sasińska, 2014)[58] One of the rare studies in this particular domain involved testing limestone samples mechanically and physically under oven and flame conditions. The stone sample behaviors in the two scenarios were compared to the state of the intact samples (fresh condition). The findings of this investigation are displayed in Table (1). The condition of exposure to direct flame has the most significant influence on the degradation of the stone samples, as the findings show that the stone samples exposed to the flame were broken, and tests could not be completed.

Table (1) Results of tests for stone samples exposed to oven and direct flame conditions [58]

Sample group	Average Porosity, (%)	Average Ultrasonic Velocity, (km/s)	Average Modulus of Rupture (MPa)
Fresh condition	12.63	5.06	4.14
Oven condition	14.38	2.00	1.65
Flame condition	—	—	—

6. Method of cooling the stone samples after heating

Researchers often use various cooling techniques to simulate the conditions of actual fire suppression on laboratory stone samples subjected to elevated temperatures. In order to simulate actual fire circumstances, researchers are interested in examining the various approaches to stone sample cooling. The fire may go out on its own without any interventions, and in this instance, it represents the air cooling the stone samples in the lab. Another method of damping a fire is to spray it with water, and this example illustrates how stone samples are cooled in a lab using water. Examining the various techniques for cooling stone samples clarifies the impact of thermal shock, which results from a sudden drop in temperature during cooling and seriously deteriorates the samples. The appropriate cooling technique for stone samples subjected to elevated temperatures is crucial in experimental investigations. Using water or a fire extinguisher might be used for the cooling procedure. The samples can also be quickly cooled by simply taking them out of the oven and letting them air cool or by cooling the samples inside the oven under carefully regulated conditions to gradually lower the oven temperature until it reaches room temperature to prevent thermal shock. One of the following techniques may be employed in the laboratory to cool stone samples that have been subjected to high temperatures:

- Air cooling down to room[12, 53, 59-60].
- Cooling by immersion in water [53].
- Cooling by spraying with water [61].
- Gradual, controlled cooling inside the oven until room temperature is reached reached [9][27][48][55].

7. Comparison of engineering behaviour of stone samples cooled at different cooling schemes

The experimental study of (Brotóns et al., 2013) [53] were interested in comparing the engineering properties of stone samples cooled with immersed water to those cooled by air at laboratory temperature, to examine the impact of various cooling techniques on stone samples exposed to high temperatures. The findings showed that, depending on the cooling technique, there were differences in the engineering properties of the stone samples heated to 600 °C. When air-cooled at room temperature, the uniaxial compressive strength fell by 34%, and when water-cooled, the percentage loss was almost 50%. Young's modulus reduces by 75% in air-cooled samples, whereas in water-cooled samples, it decreases by 78%. Conversely, for the water-cooled and air-cooled samples, the percentages of reduction in Poisson's ratio are 68% and 44%, respectively. Due to the samples' increased exposure to thermal shock, which results in the formation of cracks that impact the entire sample, the engineering properties of the stone samples have deteriorated more in the case of the water-cooling approach. The drawbacks of heat treatment are amplified when cooling is accomplished by immersion in water, as researchers have demonstrated, Water cooling reduces the stone's properties by obstructing the pores and forming micro cracks, but air cooling can only slightly increase the size of pores.

Moreover, a study of (Kara, 2021) [61] was interested in cooling the stone samples with air and the method of cooling by spraying with water for ten minutes. In this study, it is observed a loss in mass for the limestone samples cooled with air at 700 °C at a rate of 0.37%, whereas this percentage loss in mass was 0.47% for the samples cooled by spraying with water at the same temperature. This is because abrupt cooling with water causes micro fissures that alter the entire sample's pores and internal structure, which is why quick cooling (water cooling) has a greater effect on the samples.

As well-known, stone samples' properties deteriorate due to increasing porosity and cracking. looked into the impact of two different cooling techniques on stone samples that were subjected to high temperatures [60]: quick cooling with water and gradual cooling in air. The study's findings on the impact of cooling technologies on limestone's performance at high temperatures showed that porosity increased while uniaxial compressive strength and wave velocity decreased. Because of thermal shock and the formation of cracks in these stone samples, the damage was greater in the samples that were cooled in water.

8. Discussion

In this part, the most important results of previous studies regarding the effect of high temperatures on the engineering and physical properties of stone samples will be discussed.

8.1 Role of high temperature on physical and index properties

Researchers mentioned several reasons for the effect of high temperatures on the physical properties of stone samples (appearance, color, bulk density, and porosity):

- At relatively low temperatures (between 100 and 200 °C), the physical properties of stone samples undergo minor alterations. But when the temperature increases to around 400 °C, density, colour, and appearance variations are seen. Because of the small pre-existing cracks in the rocks, which are caused by the difference in the coefficient of thermal expansion of the minerals that constitute the stone samples, tensile stresses within the internal fabric of the stone samples accumulate at high temperatures, increasing the size of these small cracks [2,41,42,46].
- The red color of the stone samples rises at temperatures between 100 and 300 °C, according to researchers [12]. This is because the stones contain iron hematite. The drying of the iron compounds causes it to turn gray at 400 °C.

8.2 Role of high temperature on water transfer properties

Reviewing earlier research reveals that, while being investigated to a relatively limited extent, limestone samples' water transport capabilities are significantly impacted by exposure to high temperatures. Studies' observations indicate the following factors contribute to this phenomenon:

- The ability of stone samples to retain water is directly related to the texture and internal structure of stone samples. High temperatures lead to an increase in cracks and porosity, which causes an increase in water absorption [11].

8.3 Role of high temperature on the mechanical properties

Addressing earlier research reveals that exposure to high temperatures significantly affects the ultrasonic wave velocity, unconfined compressive strength, and limestone samples' indirect tensile strength (Brazilian test). Several researchers have noted that one or more of the following factors may be responsible for this phenomenon:

- High temperature can damage stone samples due to internal thermal stress that appears at a higher temperature, which also significantly reduces the elastic modulus [59] .

- Exposing stone samples to high temperatures causes internal thermal stresses that lead to several small cracks. As the temperature increases, these cracks gradually expand, leading to a decrease in the modulus of elasticity and a decrease in unconfined compressive strength and shear strength [21]. The thermal damage equation can also predict the percentage of damage to mechanical properties. [21] :

$$D(T) = 1 - E_{(T)}/E_{(0)} \tag{3}$$

Where:$\boldsymbol{E}_{(\boldsymbol{T})}$ is the modulus of elasticity at T °C, and $\boldsymbol{E}_{(\boldsymbol{0})}$at T=25 °

- Stone samples exposed to high temperatures lose a significant amount of moisture, experience thermal stresses, and experience expansion of the different compositional minerals in the samples. One way to put it is that minerals that expand readily are vulnerable to compressive stress, whereas minerals that expand less easily are more sensitive to tensile stress. When the heat stress, in this case surpasses the binding strength between the mineral components of the stone samples, fractures will emerge, and large cracks will significantly change the samples [54] .

- The indirect tensile strength (the Brazilian tensile test) decreases significantly with increasing temperature. High temperatures cause cracks to form and pores to increase [11][20][55]

- The research study of (Prasetya et al., 2023) [56], reported that cracks and more pores occur with rising temperatures, which results in a loss in Brazilian tensile strength. According to this finding, greater values of tensile strength are linked to higher values of fracture toughness, which are represented by the following equations:

$$K_{lc} = B.Pc.\emptyset\left(\frac{C}{R}\right) \tag{4}$$

$$\mathrm{B} = \frac{2}{\pi^{3/2}\mathrm{R}^{1/2}\mathrm{t}\alpha} \tag{5}$$

Where,

Klc: Fracture toughness, B: Geometric constant, PC: Critical force, Ø(C/R): Dimensionless stress intensity factor, R: Radius, t: Thick, and α: Contact angle.

This implies that stone models with greater tensile strength will have a lower likelihood of fractures spreading.

- Exposing stone samples to high temperatures causes internal cracks to form, reducing the ultrasonic pulse velocity.[2, 46, 62].

9. Conclusions

Conclusions concerning the main findings of the researchers after evaluating previous studies on the effect of high temperatures on the engineering behaviour of limestone samples can be summarized below.

Temperatures in the range of (100 – 200) °C slightly affect limestone samples in terms of physical and mechanical properties. Exposing the stone samples to high temperatures of up to 1000 °C leads to complete deterioration of the stone samples.

High temperatures alter the physical properties of limestone samples, resulting in a change in colour and appearance, a varied decrease in density, and an increase in porosity. The properties of the stones prior to exposure to high temperatures determine how much diversity there is in the physical properties of stone formations.

The mechanical properties of limestone are affected by high temperatures in a way that decreases indirect tensile strength, Poisson's ratio, Young's modulus, compressive strength, and ultrasonic pulse velocity values. Furthermore, high temperatures increase the porosity of limestone samples and create some cracks or increase the size of the pre-existing ones. Accordingly, limestone samples' water transfer properties (water-capillary rise, free and forced absorption) will increase and be negatively affected after exposure to high temperatures. After exposure to high temperatures, stone samples can be cooled using air, water, or laboratory-temperature cooling within an oven. How the stone samples are cooled significantly affects how the limestone samples behave in engineering.

Various cooling techniques, including air cooling, water spraying, and immersion in water, can also be used to fully comprehend how stone samples behave after exposure to high temperatures. Compared to other cooling techniques, the air-cooling approach, inside the oven at a steady rate, is thought to have the most negligible impact on stone samples' physical and mechanical properties. Nonetheless, the water-cooling technique should be highly valued from two perspectives: first, the physical and mechanical properties of stone samples cooled by water are more affected than those of stone samples cooled by other methods (thermal shock effect); in this instance, the properties of the stone samples will be distinct for the worst-case scenario. Secondly, the water-cooling technique simulates how fires are extinguished.

Finally, examining the impact of direct flame is crucial for examining how stones deteriorate in high-temperature conditions. One of the few studies on this topic revealed that the effects of high temperatures caused by fire are less than that of direct contact with fire flames.

10. Recommendations

The current review study also indicates the following recommendations:

1. Locally accessible stone resources, such as limestone and anhydrite, were used to construct many of the structures in Mosul's old city. Several of these structures were left vulnerable to fire during the most recent attempts to liberate the city. Thus, this study highly recommends investigating the engineering and physical behaviour of these stones when they are subjected to high temperatures.

2. Engineering constructions often encounter different fire severity levels (temperature intensity and fire duration). As a result, various buildings' stone components decay to differing degrees. After being exposed to fire, stones may frequently maintain a substantial portion of their resistance. Here, it is crucial to investigate whether or not these fired stones can withstand more in the future, as well as how well they function and how resistant they are to various forms of mechanical, chemical, or biological weathering. It should be emphasized that minimal prior research has addressed this kind of investigation [63]Such research on limestone samples is thus required. Accordingly, the current review strongly recommends adopting a laboratory study to determine the critical temperature, which represents a controlling factor for the durability of stones and their ability to retain a good part of their resistance after exposure to high temperatures.

3. Researchers have not extensively used the hammer and water-capillary rise tests to examine how stones deteriorate when exposed to high temperatures. It is, therefore, recommended that experiments be carried out for these tests and that fireworks be observed to affect the properties of stone samples.

4. Various types of fire extinguishing equipment are widely available. Through personal communications, the local civil defence directorate staff confirms that water can extinguish fires in stone buildings successfully. Thus, the present study recommends applying water fire extinguishers and modern methods to put out fires in the local stone buildings and making careful training efforts.

5. Following up on previous studies shows that laboratory investigation of the behavior of building stone materials directly exposed to fire flames has not been addressed much and could represent a future study plan recommended by the researchers in this study for different types of local stone materials.

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