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Possibility of producing lightweight, heat insulating bricks from pumice and H_3PO_4- or NH_4NO_3-hardened molasses binder

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Abstract

This investigation is based on the production of lightweight, heat-insulating, water-resistant or water-repellent materials from lightweight aggregates, such as pumice and/or expanded perlite, without using cement or plaster as a binder. The results of this investigation reveal that a H_3PO_4- or NH_4NO_3-hardened molasses binder with the addition of 2.5% borax could be an alternative binder for the production of lightweight, heat-insulating materials with moderate tensile strength. When these bricks were exposed to temperatures up to 825 °C, they did not lose their strength but, rather gained strength. Therefore, molasses binder could be an alternative to cement or plaster binder for construction and building materials with specific properties.

Keywords: Lightweight bricks; Pumice; Perlite; Molasses binder; Borax

1. Introduction

Various types of insulating products are used to prevent or to reduce heat and sound transfer between separated spaces. These products should have sufficient hardness to prevent punctures under normal usage conditions; have a compressive strength of at least 0.8–1.0 MN/m^2; withstand wide temperature cycles (e.g., -50 °C to 1000 °C) without a loss of or change in the physical properties; emit little or no smoke when exposed to an open flame at elevated temperatures up to 1000 °C or higher; resist organic solvents, acids and alkaline materials; be paintable with various types of decorative paints without losing its heat reflectivity; be inexpensive [1,2].

Insulating products having all these properties are accordingly in demand. Suitable materials for the production of these insulating products are lightweight materials with cellular structures, and these materials may broadly be categorised into the following groups: pumice, perlite and vermiculate.

Pumice is a lightweight volcanic aluminium silicate with a sponge-like structure formed by the expansion of gases when molten lava rapidly cools. Pumice comprises a group of materials having a similar origin and physical structure, such as pumicite, volcanic cinders, scoria and volcanic tuff. Pumice is always associated with recent volcanic activity, and it may show acidic and basic properties depending on its SiO_2 and CaO/MgO contents, respectively. Pumice is generally more acidic, and cinders, scoria and tuff are more basic. Pumice has a low bulk density, ranging from 480 kg/m^3 to 960 kg/m^3, a high strength-to-weight ratio, low thermal conductivity and low sound transmission characteristics. These features make pumice desirable for use as building material for lightweight bricks, blocks and aggregate for concrete and plaster [3].

Perlite is a glassy volcanic aluminium silicate that contains 2–5% combined water that expands 10–30 times its original volume when heated to temperatures between 760 °C and 1150 °C, depending on the composition of the raw material. The volatilisation of the combined water during the shock heat treatment expands the hot, softened ore into foam that solidifies into a lightweight, cellular aggregate with bulk densities ranging between 80 kg/m^3 and 240 kg/m^3. The resulting expanded product has a variety of industrial- and construction-related applications because of its lightweight, porosity, non-flammability, thermal insulation, noise control and non-toxicity.

Exfoliated vermiculite and phlogopite, expanded obsidian, expanded clay, and so forth are also porous. Lightweight and

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insulating materials are widely consumed for building-related uses consisting of concrete aggregate, plaster, formed product, masonry and cavity fill [3].

Although their heat- and sound-insulating properties are comparatively better than pumice, all of the above-mentioned materials have some disadvantages when compared with pumice. The main disadvantages are their high cost because they require a high-temperature heat treatment for their expansion, and their low mechanical strengths because of their very low densities. Pumice is a natural material, possessing adequate heat- and sound-insulating properties, and it is readily available and is relatively cheap. From an economical point of view, pumice is preferred to the above-mentioned materials, especially in the construction industry. During the preparation of lightweight and insulating products from these materials, cement, plaster, alkali silicates (water glass) and polymeric materials of various types are used as binding agents. Moreover, fibres of organic and inorganic origins are used for reinforcing purposes in some formulations.

In construction, pumice is usually mixed with Portland cement or calcium aluminate cement and formed into bricks, panels, blocks, fire doors, and so forth. In coating applications, organic binders, such as asphalt, synthetic polymers, pulping sulphite waste liquor and starch, may be used together with cement to enhance the adhesion of the resultant coating to the surface of the substrate. Sodium silicate, generally in the form of aqueous solutions containing 40% $Na_2Si_3O_7$, solid sodium silicate or borax are also used as binding agents together with cement to improve the adherence, flame resistance and water resistance of these products. In all of these applications, cement and/or plaster are always used as the main part of the binding agent.

Thermal conductivity depends upon the pore structure of the lightweight aggregate, density of concrete and cement paste matrix. Thermal conductivity increases linearly with increases in the density of concrete. As long as the cement and/or plaster are used as the main binding agents for concrete production, the thermal conductivity of the concrete cannot be reduced below a certain limit because a decrease in the density will result in a substantial decrease in the mechanical properties [4].

In addition, the mechanical properties of concrete are also seriously affected by increases in temperature. The deterioration in the mechanical strength of concrete begins as low as 200 °C and becomes more pronounced above 400 °C. When cement and/or plaster are used as a binding agent, a greater danger of collapse exists for concrete buildings in the event of fires. Therefore, the construction materials, especially for buildings, should have low thermal conductivity and should be able to withstand high temperatures, e.g., they should not lose their strength or should gain some in case of fire [5].

The production of heat- and sound-insulating bricks of high tensile strength from pumice and phenolic resin binders were investigated in detail. The results indicate that bricks with tensile strength of 43.37 MN/m^2 could be produced without using cement and/or plaster. Although producing waterproof bricks with high tensile strength from pumice and phenolic resins is possible, the main drawback of this process is the high cost of the phenolic resins to be used as the binder. To reduce the cost of the binder, relatively cheap and readily available alternative binder or binders are needed [6].

When H_3PO_4-hardened molasses was used as a binder for the production of smokeless fuel [7–11] or metallurgical-quality formed coke from anthracite fines and/or coke breeze, the resulting briquettes were highly water resistant and strong curing at 200 °C for 2 h. This type of binder requiring H_3PO_4 hardener was found to be unsuitable for the production of formed coke because incomplete extraction of phosphorus from the coke causes serious weakening in the structure of the steel [12]. However, this binder might be utilised in the production of bricks from pumice. In addition to H_3PO_4-hardened molasses binder, NH_4NO_3-hardened molasses [13] binder resulted in strong and highly water resistant briquettes. Therefore, NH_4NO_3-hardened molasses might also be used as a binder in the production of lightweight heat- and sound-insulating bricks from pumice. Pumice and perlite bricks of low thermal resistance and relatively high crushing strength (ranging from 0.49 to 5.59 MPa were produced with boron-containing materials, such as tincalconite, sodium tetraborate decahydrate and anhydrous (fused) sodium tetraborate by heat treatment at temperatures ranging from 650 °C to 900 °C without using any other inorganic or organic binders. Information about the green crushing strengths of these bricks was not given [3].

The aim of this investigation is based on the production of lightweight and relatively strong, heat- and sound-insulating bricks from pumice and/or perlite with H_3PO_4- and NH_4NO_3-hardened molasses binders. The high-temperature behaviour of these bricks containing pure sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) is also studied in detail. The effects of H_3PO_4 and NH_4NO_3 hardener and the addition of sodium tetraborate decahydrate (borax) on the tensile strength of the bricks are determined.

2. Experimental

The process for producing building materials with heat- and sound-insulating properties from pumice and from a blend of pumice and expanded perlite with different binders is illustrated in Fig. 1.

The city of Kayseri in Turkey is located near the volcanic mountain Erciyes. A large reserve of pumice is located around the mountain because of emerged magma. The X-ray fluorescence (XRF) analysis of the pumice and the expanded perlite provided by Etiper (perlite expanding company in Izmir, Turkey) is shown in Table 1. The molasses supplied by a sugar factory in Kayseri is given in Table 2. Commercially available technical grade borax, NH_4NO_3 and H_3PO_4 were used.

2.1. Pumice preparation

Pumice (100 kg) was taken from the pumice mine near the village of Kamber, which is approximately 25 km from Kayseri. The raw pumice was poured into water and floated. The light-weight part was separated. After drying, the floated pumice was crushed and ground to pass through a 1-mm sieve. To avoid a large amount of ultrafine particles, a small portion of

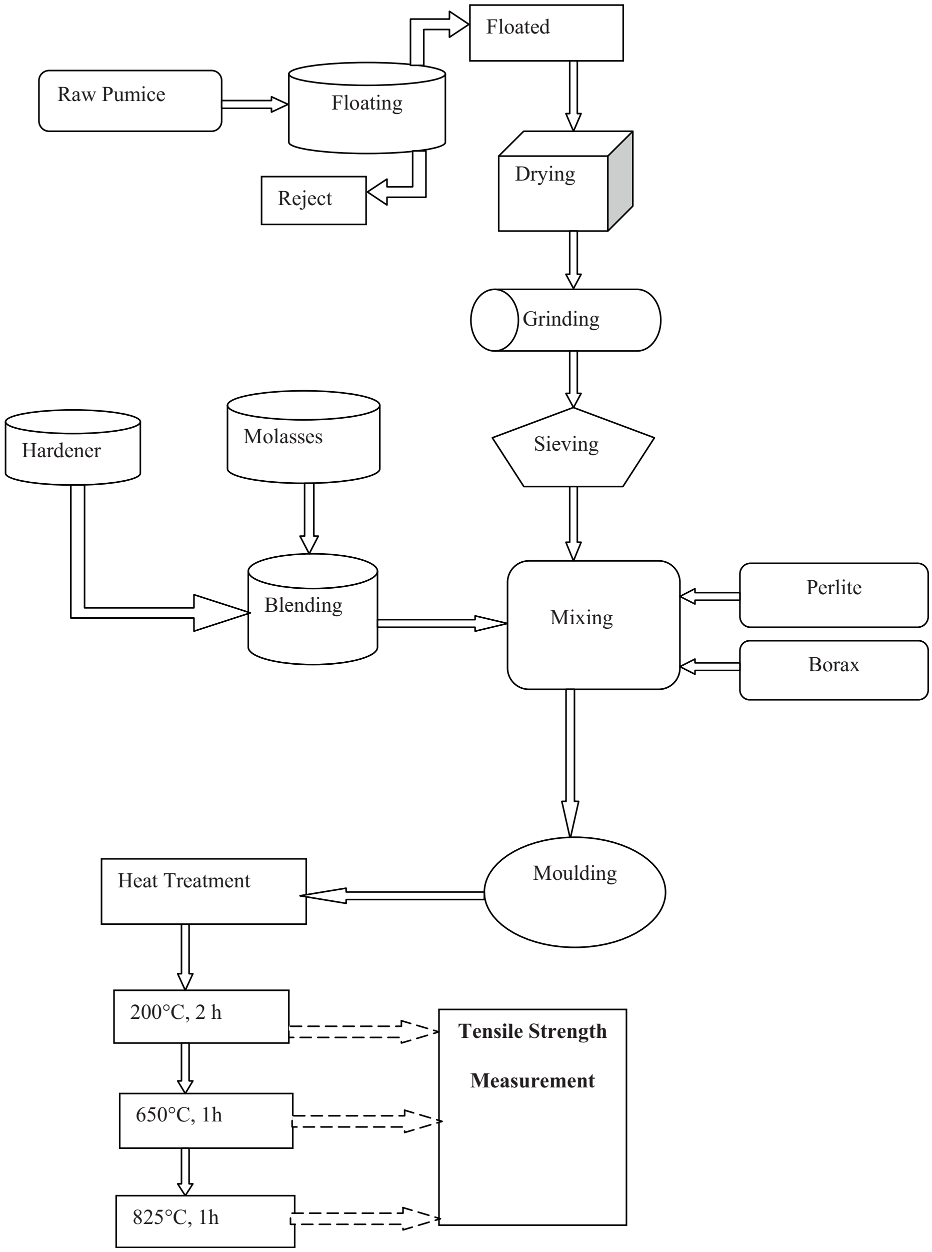

Fig. 1. The scheme of the process for producing building materials from pumice and expanded perlite with different binders.

the dried pumice was crushed and ground for 2–3 min. The entire oversized fraction retained on the 1-mm sieve was sieved off, returned to the grinder and then re-ground. This cycle was repeated until the entire floated sample was ground and sieved. Approximately 90 kg of sample was prepared, mixed properly and then divided by quartering into 25 kg fractions. The fractions were then packed into plastic bags.

Table 1
The main components of the pumice and perlite.

Component %	Pumice	Perlite
SiO_2	63	74
Al_2O_3	16	14
Na_2O	3	3
K_2O	3	5
MgO	0.7	0.5
CaO	2.6	0.5
Fe_2O_3	4	1
Grain diameter	0–1 mm	0–2 mm

2.2. Blending and brick preparation

Our preliminary experiments confirmed that the order of addition of the starting materials was important, e.g., simultaneous mixing of pumice, molasses, catalysts and water did not

Table 2
Analysis of molasses.

pH (20 °C)	7.93
Bulk density (g/cm^3)	1.218
Polarization (%)	48.86
Brix (%)	81.50

give bricks with the desired properties [14]. Treatment with pumice was performed first. A sufficient amount of water was then added to fill all of the pores prior to binder addition. Mixing with binder, which contained the catalyst to form the formable mixture, was next. Borax, dissolved in water, was then added. If molasses were added prior to the water, then the pores would be filled with molasses. As a result, part of the binder would be needlessly consumed for filling the open pores instead of encapsulating the particles of pumice and/or perlite, and more binder would be necessary to produce bricks of the same tensile strength. The pumice, water, molasses-containing catalyst and dissolved borax were weighed separately, and their stepwise addition and mixing were carried out in a shallow dish that was large enough to allow any variable, to be tested by pressing ten identical bricks at a time.

Each brick was made by pressing 20 g of the mixture in a 23-mm internal-diameter steel mold. In case the brick prepared from the blend containing 20% expanded perlite, the amount of the mixture was reduced to 10 g. The pressure was applied to the mixture by means of a closely fitting steel plunger under a hydraulic press until the same heights of the bricks (45 ± 1 mm) were obtained.

When the bricks were prepared with 5% borax as the sole binder, the open pores of the pumice and/or perlite were filled with a sufficient amount of water, and the dissolved borax was added and mixed homogenously. Bricks with the same weight and dimensions as the molasses-bonded binder containing catalysts were also prepared from the borax binder alone.

2.3. Heat treatment

To determine the effect of the heat treatment temperatures, ranging from 200 °C to 825 °C, on the tensile strengths of bricks to which the bricks may be exposed (e.g., in the case of fire), the bricks were cured at 200 °C for 2 h. Some of the cured brick were then pyrolised at 650 °C for 1 h and then at 825 °C for 1 h in an air-circulating muffle furnace. After cooling, the tensile strengths of the ten bricks, representing each variable, were measured unless otherwise stated.

2.4. Determination of tensile strength

The tensile strength of each brick was measured by a diametrical compression test. The details are described by Blayden et al. [15]. Briefly, the cylindrical surface of the brick was placed on a horizontal metal plate and assembled onto the hydraulic press. A compressive load was then applied across the diameter of the brick by reducing the distance slowly between two metal plates, maintained parallel to the plunger of the hydraulic press. When the applied stress reached the tensile strength, the load cell signal suddenly dropped as the sample fractured because of the tensile stress along the vertical plane passing through its axis. The relation between the applied load (w) and the tensile stress (P) is given by

$$P = \frac{2w}{\Pi Dt},$$

where D is the diameter and t is the height of the brick [16–20]. The brick strengths reported here are typically the arithmetic means of ten measurements unless otherwise stated. The standard deviations of the mean of the strength are also reported.

3. Results and discussion

3.1. General

When cement and/or plaster are used as the main part of the binder for producing concrete or bricks for construction work, the bricks lose approximately 25% of their original strength when heated to 300 °C and approximately 75% when exposed to 600 °C. The reason for the loss in their strength with the rise in temperature may be speculated as follows. When concrete or bricks are prepared from cement and/or plaster and then subjected to high temperatures, water, which is chemically bound in hydrated cement or plaster, becomes free to migrate into the pores. This migration is due in part to the lower permeability of these materials, which limits the ability of moisture to escape from the pores. This results in built-up pore pressure. As the temperature increases, as in the case of fire, the pore pressure also increases. This increase in vapour pressure continues until the thermal stress becomes sufficiently large to cause explosive spalling of the heated concrete or bricks. Explosive spalling weakens the structure of these materials and results in the loss of strength [21].

Suggested techniques for mitigating the risk of explosive spalling include: (1) increasing the thermal diffusivity of these materials with mineralogically suitable aggregate to minimise the thermal gradient, (2) increasing the open microporosity by utilising pumice or perlite to lower the water pressure and (3) insulating the structure to lower the heating rate to facilitate the progressive release of water vapour. Experimental validation is needed before modelling tools can be used for parametric studies of the performance of these materials when exposed to fire [21].

The weight of the material used in buildings is of great importance in the event of earthquakes. Reduced dead load obtained by utilising lightweight material results in a decrease in the cross section of columns, beams, walls and foundations. Furthermore, lightweight materials decrease the induced seismic loads and reduce the risk of earthquake damages to structures because the earthquake loads influencing the structure and buildings are proportional to the mass of the structures and buildings [22].

The sound and thermal conductivity of the material are also important from an energy-saving and energy- and sound-contamination point of view. Both are related to the mineralogical character and density of the materials, i.e., crystalline silica is approximately 15 times more conductive than natural amorphous silica, such as pumice [23].

The aim of this investigation was to produce lightweight bricks from pumice and molasses binder.

3.2. Effect of H_3PO_4 and NH_4NO_3 hardeners

To define the effect of H_3PO_4 and NH_4NO_3 hardener on the water resistance, tensile strength and behaviour of the bricks at high temperatures, 50 cylindrical bricks of approximately 20 g each were prepared from pumice and molasses binder.

The composition of each bricks was adjusted to contain 85% (w/w) pumice, 12.5% (w/w) molasses and 2.5% (w/w) hardener. The amount of water to fill the pores of the pumice was kept constant at 20 g for 100 g of this mixture. The amount of pumice sufficient to prepare 50 bricks was first weighed and mixed with water to fill the pores of the pumice. Molasses binder containing hardener was then added and mixed thoroughly until all of the particles of pumice were encapsulated by the binder homogenously. Cylindrical bricks of same height and diameter were prepared by adjusting the movement of the hydraulic press.

After preparing 80 bricks (40 of them prepared from H_3PO_4 hardener and 40 of them from NH_4NO_3 hardener), each brick was weighed and measured. Sixty of the bricks were placed in an air-circulating muffle furnace and heated at the targeted temperatures for the specified times: 200 °C for 2 h, 650 °C for 1 h and 825 °C for 1 h. Ten bricks with the H_3PO_4 hardener and ten bricks with the NH_4NO_3 hardener were kept in desiccators for future tests. Ten bricks from each type were removed from the oven at the targeted temperature after the specified time and allowed to cool to room temperature. These bricks were then weighed and measured for possible mass and size losses. Tensile strength tests were performed on all of the bricks.

The test results in terms of tensile strength with respect to temperature are summarised in Figs. 2–4 show the relationship between the weight loss %, contraction % and heat treatment of temperatures of these two types of bricks, respectively.

For both types of bricks, a similar trend is observed: an initial gain in tensile strength at 200 °C, strength loss between 200 °C and 650 °C and a permanent gain of strength at temperatures above 650 °C. Comparisons between the bricks produced from the H_3PO_4- and NH_4NO_3-hardened molasses binder showed different tensile strengths at different temperatures. The tensile strength of the bricks prepared with the NH_4NO_3-hardened binder was higher than the bricks prepared from the H_3PO_4-hardened binder when they were cured at 200 °C for 2 h. However, the bricks prepared with the H_3PO_4-hardened binder had greater tensile strength following heat treatments at 650 °C for 1 h and at 825 °C for 1 h.

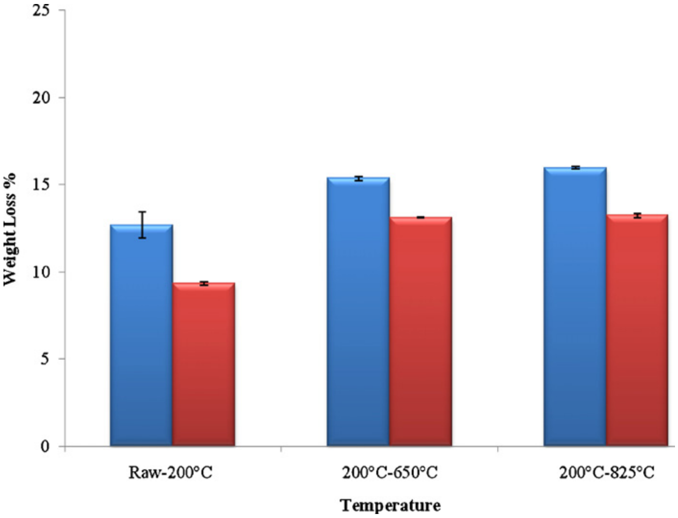

Fig. 3. Weight loss % of the molasses-bonded pumice bricks with the respect to temperatures (first column: 2.5% NH_4NO_3 hardener; second column: 2.5% H_3PO_4 hardener).

This difference in the tensile strength of the bricks that were cured at 200 °C for 2 h can be attributed to the differences in the actions of these hardeners. Generally, NH_4NO_3 linearly crosslinks whereas H_3PO_4 forms a three-dimensional, crosslinked molasses structures. The three-dimensional crosslinked structures cause the bricks to be more brittle than the linearly crosslinked bricks, so the tensile strength of the H_3PO_4-hardened molasses bonded bricks have lower tensile strength than the NH_4NO_3-hardened molasses-bonded bricks. Similar results were also obtained when these hardeners were used to

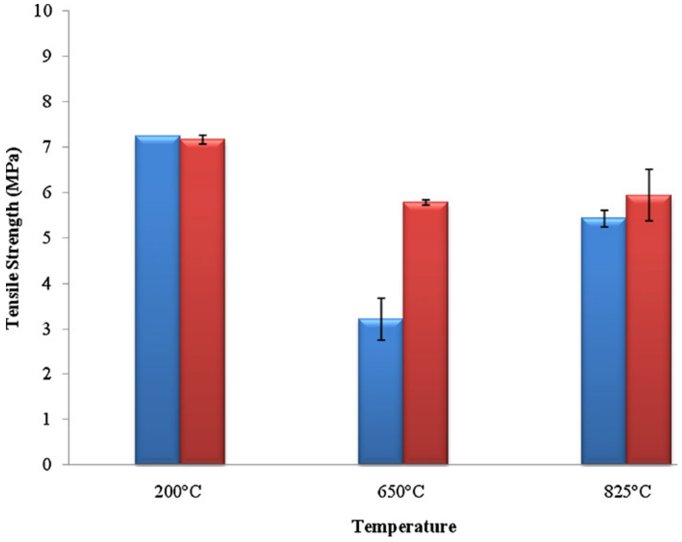

Fig. 2. The tensile strength of the molasses-bonded pumice bricks with the respect to temperatures (first column: 2.5% NH_4NO_3 hardener; second column: 2.5% H_3PO_4 hardener).

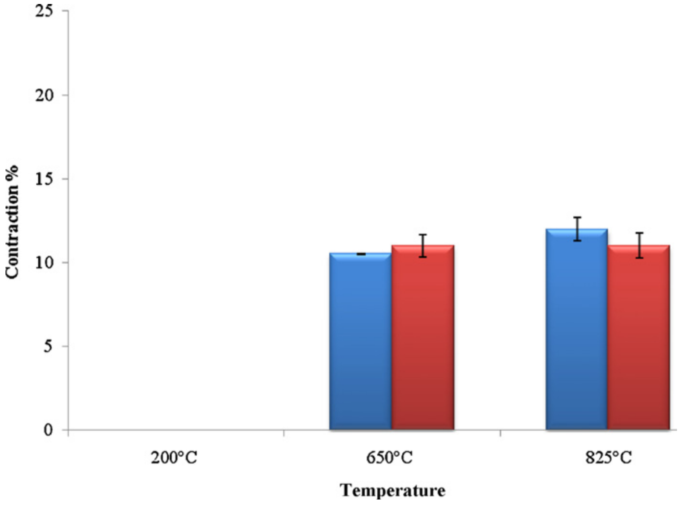

Fig. 4. Contraction % of the molasses-bonded pumice bricks with the respect to temperatures (first column: 2.5% NH_4NO_3 hardener; second column: 2.5% H_3PO_4 hardener).

harden the molasses binder for the production of anthracite and coke breeze briquettes [13].

The H_3PO_4-hardened molasses resulting in relatively stronger bricks than the NH_4NO_3-hardened molasses when they were heat treated at temperatures of 650 °C and 825 °C may be because H_3PO_4 improved the fire resistance of the binder. The decomposition of NH_4NO_3 provides oxygen for burning the binder present within the pores of the bricks, whereas the oxygen in the air in the furnace may not be able to penetrate through the surface of the brick This situation may weaken the structure of the molasses structure remaining in the bricks and may causes some reduction in the tensile strength.

The results shown in Fig. 3 confirm that the weight loss % of the NH_4NO_3-hardened molasses-bonded bricks is relatively higher than the weight loss % of the H_3PO_4-hardened molasses-bonded bricks when they were heat treated at 650 °C and 825 °C for 1 h, respectively. The % contractions were almost the same at all of the heat treatment temperatures ranging from 200 °C to 825 °C (see Fig. 4).

3.3. The role of borax

The utilisation of borax as the sole binder for producing lightweight, heat-insulating, high compressive strength and water-insoluble material by heat treatment at temperatures between 650 °C and 900 °C was patented [3]. In this patent, the bricks were produced from a mixture containing 96.8% (w/w) pumice and 3.2% borax binder. The bricks had a compressive strength of 2.16 MPa when heat treated at 825 °C for 15 min. The patent was not clear on the green strength, the variation of the strength when heat treated at temperatures lower than 825 °C and on the size loss of the bricks. The patent clearly indicated that borax could be used as a binder in the production of lightweight bricks from pumice.

To confirm the possibility of producing bricks from pumice by utilising borax as a sole binder and to determine the effect of the addition of borax on the properties of bricks prepared from pumice and molasses binder with or without H_3PO_4 or NH_4NO_3 hardener, the following experiments were performed. For every tested variable, 40 bricks were prepared from a mixture containing the following:

1) 95% (w/w) pumice and 5% borax, 85% (w/w) pumice, 12.5% molasses and 2.5% borax.
2) 82.5% (w/w) pumice, 12.5% molasses, 2.5% H_3PO_4 and 2.5% borax.
3) 82.5% (w/w) pumice, 12.5% molasses, 2.5% NH_4NO_3 and 2.5% borax.

The order of the addition of the component was the same as previously described. Pumice was mixed with water until all of the pores were filled with water. The addition of the binder followed, and it was mixed well until all of the pumice particles were encapsulated homogeneously. In all of the preparations, whether borax was used as the sole binder or as one of the hardeners with H_3PO_4 or NH_4NO_3, borax was added at a concentration of 50% (w/w) in water. After mixing all of these components, the damp mixture was compressed to form the bricks with a mass of approximately 20 g, a diameter of 23 mm and 45 mm in height. The bricks were then placed on a board in a manner such that none of the bricks was broken because the green bricks were very weak could be distorted or broken into pieces with finger pressure.

After weighing and measuring the dimensions of the bricks, 120 bricks (30 from each type) were placed into an air-circulating muffle furnace. The same heat treatment procedure was performed as described earlier. Ten bricks of each type were removed from the oven at the targeted temperature after the specified time and then weighed and measured for mass and size losses. After cooling to an ambient temperature, their tensile strengths were measured. The results in terms of variation of tensile strength % contraction and weight loss % of the bricks with respect to temperature are shown in Figs. 5–7, respectively.

The results in Figs. 2 and 5 reveal similar tensile strength patterns with the tensile strength being higher when cured at 200 °C for 2 h, decreasing to a minimum at 650 °C and increasing again at 825 °C. An exposure temperature of 650 °C appears to be the level that marks the highest rate of strength loss and weight loss for all of the bricks investigated. The strength loss might be due to the extensive disruption of the complex assembly of chemical bonds developed in the binder and/or between the binder and pumice during curing at 200 °C with the rise of the treatment temperature up to 650 °C.

When borax was used as the sole binder for the production of lightweight, heat-insulating and highly water-resistant bricks from pumice, the resultant bricks possessed the lowest tensile strengths among the binders investigated, independent of the temperatures to which the bricks were exposed (Fig. 5). These bricks had almost no strength (0.89 MPa) even after curing at 200 °C for 2 h. This result indicates that borax alone did not act

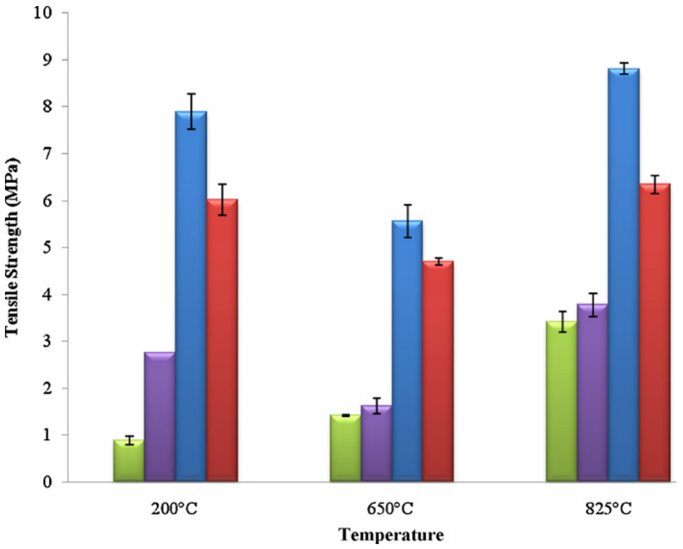

Fig. 5. The tensile strength of the molasses-bonded pumice bricks with the respect to temperatures (first column: 5% borax; second column: 12.5% molasses–2.5% borax; third column: 12.5% molasses–2.5% NH_4NO_3–2.5% borax; fourth column: 12.5% molasses–2.5% H_3PO_4–2.5% borax).

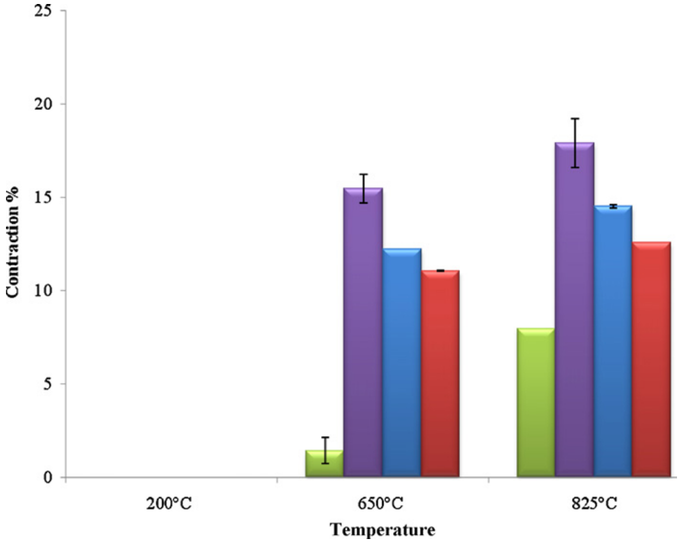

Fig. 6. Contraction % of the molasses-bonded pumice bricks with the respect to temperatures (first column: 5% borax; second column: 12.5% molasses–2.5% borax only; third column: 12.5% molasses–2.5% NH_4NO_3–2.5% borax; fourth column: 12.5% molasses–2.5% H_3PO_4–2.5% borax).

to bind the pumice particles, especially at low temperatures, e.g., temperatures below 200 °C.

Permanent increases in the tensile strength of the bricks were observed when they were exposed to heat treatment temperatures of 650 °C for 1 h or 825 °C for 1 h. This strengthening might be due to the decrease in the melting point of the pumice caused by the presence of borax adjacent to the surface of the pumice particles. Borax is active, readily fusible, acid flux. Since the presence of borax even in small amounts lower the temperature of slag formation appreciably and promotes a quiet and orderly fusion, it is used universally in fire assaying [24]. The small amount of borax addition into the bricks, may play the similar role as in the fire assaying. Therefore, the increase in the tensile strength of the bricks with heat treatments above 650 °C could be attributed to the sintering or fusion of the surface of the pumice particles that resulted in a decrease in the melting point of pumice because of the presence of borax. The thickness of the fused zone that adheres the particles to each other increases with rises in temperature and the length of the time that the bricks are kept at those temperatures in the muffle furnace. This increase in the fused zone might be the main governing factor for the development of strength in bricks. Higher temperature and the longer durations result in thicker fused zones. Stronger bonds are developed between the particles, and the tensile strength of the resultant bricks increases. The rise in the tensile strength of the bricks heat treated above 650 °C should be attributed to the fusion of the pumice particles to develop inorganic bonds rather than organic bonds. The addition of borax helps these types of bonds to develop between the pumice particles by reducing their melting points.

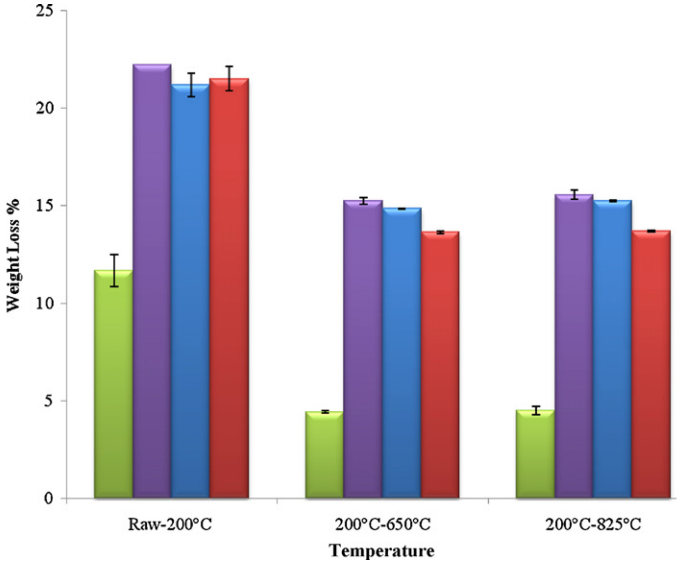

Fig. 7. Weight loss % of the molasses-bonded pumice bricks with the respect to temperatures (first column: 5% borax; second column: 12.5% molasses–2.5% borax; third column: 12.5% molasses–2.5% NH_4NO_3–2.5% borax; fourth column: 12.5% molasses–2.5% H_3PO_4–2.5% borax).

The possibility of using borax alone as a hardener rather than binder was also investigated by preparing bricks containing 85% (w/w) pumice, 12.5% (w/w) molasses and 2.5% (w/w) borax. Bricks were produced by following the same brick preparation procedure and were heat treated at the same temperatures and time intervals. Fig. 5 presents the tensile strengths of these bricks, and the second column shows the results of each heat treatment temperature. The tensile strengths of the resulting bricks were relatively higher after all of the heat treatment temperatures than the bricks prepared from borax binder alone. However, even after curing at 200 °C for 2 h, the bricks did not gain adequate strength and water resistance. Therefore, borax alone was found to be an unsuitable hardener for molasses binder.

The third and fourth column diagrams in Fig. 5 indicate the tensile strengths of the bricks prepared from molasses binder containing 2.5% H_3PO_4 or NH_4NO_3 hardener together with 2.5% borax and exposed to earlier described heat treatment procedure. These diagrams clearly indicate that when 2.5% borax was added into both types of bricks during their preparation, the tensile strengths of the NH_4NO_3-hardened molasses-bonded bricks were always higher at all of the temperature studied than those of the identically prepared and heat-treated H_3PO_4-hardened molasses-bonded bricks. The results shown in Fig. 2 were without borax addition, and the NH_4NO_3-hardened molasses binder resulted in bricks of higher tensile strength than the H_3PO_4-hardened molasses binder only when they were cured at 200 °C for 2 h. While at higher temperatures of 650 °C and 825 °C, the bricks treated with H_3PO_4-hardened molasses binder had greater tensile strength. If the tensile-strength results in Figs. 2 and 5 are considered together, then they suggest that the addition of the same amount of borax improves the tensile strength of both types of the brick. However, borax addition improved the tensile strength of the bricks prepared from NH_4NO_3-hardened molasses-bonded bricks more than H_3PO_4-hardened molasses-bonded bricks. Additionally, borax addition did not substantially enhance the tensile strength of the bricks prepared from molasses containing

H_3PO_4 hardener. As indicated in the second column of Fig. 5, the addition of the same amount of borax to the molasses binder without any of these hardeners had almost no effect on the tensile strength of the bricks.

Comparing the results in Figs. 4 and 6, the % contraction of the bricks increased because of the reduction in the melting point of the pumice caused by the presence of borax. This result means that the addition of borax causes pumice particles to melt and makes the bricks shrink, which increases the density of the bricks. Thus, the increase in density results from an increase in the thermal conductivity because thermal conductivity changes linearly with changes in the density. These results show that borax alone is not a suitable binder for the production of lightweight, heat-insulating relatively strong bricks unless heat treated above 650 °C.

Borax had little or no binding effect in preparing the pumice bricks. When borax was added into the NH_4NO_3-hardened molasses-bonded bricks; however, it may react with NH_4NO_3 to develop a new chemically structured hardener that may increase the number of bonds developed in the molasses binder without changing its linearly crosslinked structure. As a result, when these bricks were exposed to high temperatures, the amount of molasses remaining as carbon residue, especially inside of the bricks, increased. Hence, the NH_4NO_3-hardened molasses-bonded bricks containing 2.5% borax showed the greatest tensile strength among all of the bricks investigated. This speculation may be supported by comparing the weight losses of the bricks, shown in Figs. 3 and 7, prepared from molasses binder containing no NH_4NO_3 hardener and 2.5% borax, containing 2.5% NH_4NO_3 with no borax and containing 2.5% NH_4NO_3 with 2.5% borax. The differences in the weight loss % of these three types of bricks were not substantial for any of the temperatures to which they were exposed. The molasses containing no NH_4NO_3 with 2.5% borax had the greatest weight loss %, and the molasses containing 2.5% NH_4NO_3 hardener with 2.5% borax had the smallest weight loss %. The presence H_3PO_4 hardener resulted in the bricks with the lowest weight loss % among the studied bricks. The addition of 2.5% borax into the bricks prepared from molasses binder containing 2.5% H_3PO_4 caused a slight decrease in the weight loss % of the bricks.

The increase in the tensile strength of the bricks by the addition of 2.5% borax should be attributed to the fact that the addition of borax did not act as a binder, but it was involved in increasing the fire resistance of the crosslinked molasses binder in the bricks, which resulted in more carbon residue remaining in the bricks during high temperature treatments.

Theoretically, if the high-temperature, heat-treated bricks experienced lower weight loss, which is an indication of carbon residue remaining in the bricks, then one should expect that their tensile strength should be higher than the bricks with greater weight losses. When 2.5% borax was added to both H_3PO_4- and NH_4NO_3-hardened molasses-bonded bricks, the H_3PO_4-hardened molasses-bonded bricks possessed lower weight loss and had lower tensile strength than the NH_4NO_3-hardened molasses-bonded bricks. These results are inconsistent with the above theory.

The explanation for this divergence from the theory could be that H_3PO_4 results in a highly branched, three-dimensional crosslinked structure in the molasses binder, while NH_4NO_3 produces linearly crosslinked structure when the bricks were cured at 200 °C for 2 h. Highly branched, three-dimensional crosslinked structure makes the resultant bricks more brittle than the linearly crosslinked structure, which possesses higher elasticity. When loads were applied during the tensile strength measurements, the stress developed in the bricks can cause the brittle bricks to crack easier than the elastic structure ones. Long linear chains and less branching increase the molecular movement of the binder, which may dissipate energy throughout the bricks. Therefore, the H_3PO_4 hardener develops stronger bonds, but the brittleness of the bricks lowers their tensile strengths.

The tensile strength of high-temperature treated bricks correlates roughly linearly with the tensile strength of the cured bricks, even if some of the binder burns because of the presence of air [25]. The extensive disruption of the complex assembly of chemical bonds, which are created during curing and which contribute to the brick strength from the initial pattern of the bonding, occurs. Therefore, heat treatments of the bricks will create a binder coke residue in the same position that the binder occupied during the curing stage. The highly branched, three-dimensional crosslinked structures result in lower weight loss. The linearly crosslinked structures give relatively higher weight loss. However, the brittleness of the highly branched structure causes the bricks to have lower tensile strength.

3.4. Water-repellent coating

The low-density granular materials possess many open and closed pores, and the new open pores are also developed during crushing and grinding. When these materials are used to produce lightweight heat-insulating materials (e.g., panels and bricks) additional open and/or closed pores emerge because of the evaporation of water and the decomposition of the binder during the drying and curing process. Therefore, the low-density granular materials must be covered with water-repellent coating materials to prevent the granules and particles from absorbing water and to provide protection from water penetration through these open pores. Otherwise, the density and thermal conductivity of the materials would increase, and their tensile strength would be reduced because of cracks that could develop as a result of seasonal temperature changes.

Different types of coating materials are available, such as asphalt, asphaltite, wax and stearic acid. However, these organic hydrophobic materials are not preferred in elevated-temperature applications. Silanes, silicones, siloxanes and their derivative are preferred because of their heat stability and their degree of hydrophobicity, even when used in small, quantities [26,27].

In this investigation, an alcohol solution of polyalkylsiloxane was used as the water-repellent material. Pumice particles were coated homogenously with this solution. The amount of this solution was adjusted to be 1% (w/w) polyalkylsiloxane remaining in the raw brick. The pumice and polyalkylsiloxane

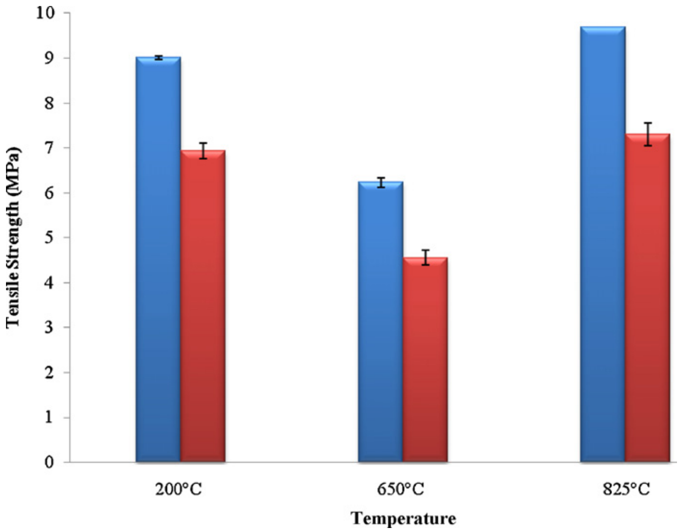

Fig. 8. The tensile strength of the molasses-bonded polyalkylsiloxane coated pumice bricks containing 2.5% borax with the respect to temperatures (first column: 2.5% NH_4NO_3 hardener; second column: 2.5% H_3PO_4 hardener).

mixture was dried in rotary evaporator until all of the alcohol mixture evaporated. Two types of bricks were prepared from these coated pumice particles by utilising 2.5% H_3PO_4 or 2.5% NH_4NO_3–hardeners containing molasses binders. Borax (2.5%) was added into this mixture to compare its effect with the results obtained from the uncoated pumice bricks with the same amount of these hardeners and borax. Molding, curing and heat treatment procedures were the same previously described.

The tensile strengths of these bricks at the same heat treatment temperature are shown in Fig. 8. Polyalkylsiloxane improved the tensile strengths at all of the heat treatment temperatures. This result shows that polyalkylsiloxane acted as a binder and as a water-repelling agent. When the brick were coated, the amount of water absorption was reduced significantly. The bricks that were cured at 200 °C for 2 h could float on water. At higher temperatures, the heat-treated bricks lost some of their water-repellent properties because of the decomposition of the molasses binder creating new open pores so that their water-repelling properties were reduced to some extent. Therefore, after floating for a short time, these bricks would sink. Instead of coating the pumice particles as above, the bricks were coated after curing or after exposing them to high temperature by spraying the coating solution onto the surface of the bricks to produce the water-repellent coating. This method could also be applied to the newly emerged surfaces of bricks due to breakage when placing them into the walls of buildings. However, the water-repellent coating would create additional costs for the process.

3.5. Plaster or cement binders

To compare the behaviour of the molasses with cement or plaster as binders, the pumice bricks were prepared from 60% (w/w) plaster or Portland cement binders with a sufficient amount of water. The tensile strengths of these bricks are given in Fig. 9.

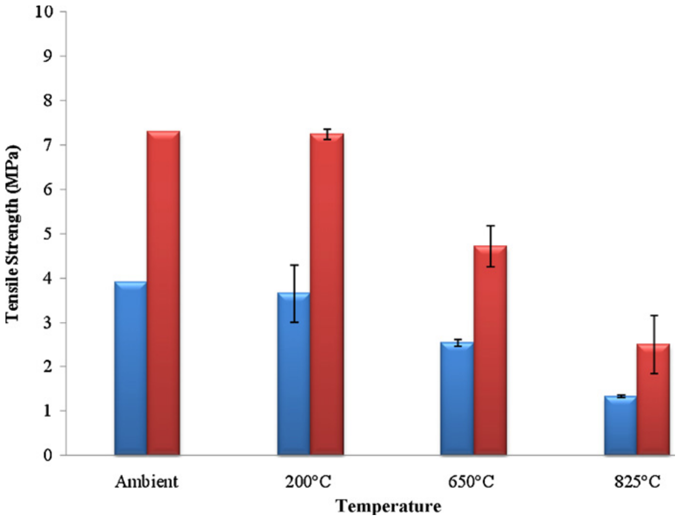

Fig. 9. The tensile strength of the pumice bricks with the respect to temperatures (first column: 60% cement binder; second column: 60% plaster binder).

After 7 days of curing in a humid environment at ambient temperature, the tensile strength of the plaster-bonded pumice bricks was found to be higher than the cement-bonded bricks. The strength of both types of decreased drastically as the treatment temperatures increased above 200 °C. These results demonstrate that in the event of fire, cement or plaster-bonded brick could lose their strengths, and this loss of strength might cause the building to collapse. In contrast, H_3PO_4- and NH_4NO_3-hardened molasses-bonded bricks containing 2.5% borax gain strength with high temperature treatments.

3.6. Blending of perlite with pumice

The results obtained in this investigation show that lightweight, heat-insulating, water-resistant bricks of the highest tensile strength from pumice could be produced by utilising molasses containing 2.5% NH_4NO_3 hardener and by the addition of 2.5% borax. These bricks, if exposed to high temperatures (e.g., a fire), would not lose their strength and may gain some strength. Thus, these bricks meet the goals of this investigation. If necessary, the thermal conductivity of the bricks can be improved by replacing part of the pumice with expanded perlite and/or expanded vermiculate.

The results of the prior investigation showed that the addition of more than 20% (w/w) perlite into concrete reduced its strength to an unacceptable level [28]. In this investigation, the bricks were prepared by replacing 20% (w/w) perlite with pumice, and the other ingredient and conditions were kept constant to prevent the bricks from losing their strength drastically.

NH_4NO_3- and H_3PO_4-hardened molasses-bonded bricks containing 2.5% borax were prepared by replacing 20% perlite with the pumice in the bricks. To avoid breaking the perlite particles by the pressure applied during molding, the amount of mixture used for the production of each green brick was reduced from 20 g to 15 g, but their dimensions were kept constant. This reduction in weight resulted in a 25% decrease in the density of the perlite-containing green bricks. The tensile

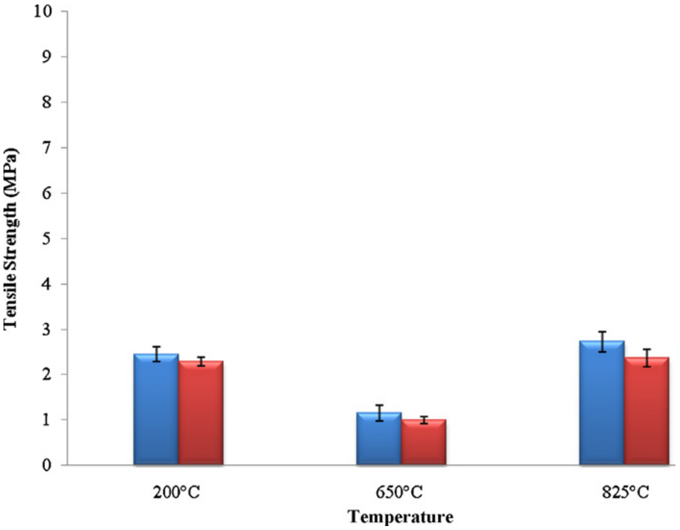

Fig. 10. The tensile strength of the molasses-bonded pumice bricks containing 20% perlite, 2.5% borax with the respect to temperatures (first column: 2.5% NH_4NO_3 hardener; second column: 2.5% H_3PO_4 hardener).

strength of the bricks in relation to the heat treatment temperatures is given in Fig. 10.

The trend for tensile strength development as a function of the treatment temperature revealed the same pattern as that of the bricks containing no perlite. The maximum tensile strength was obtained when the bricks cured at 200 °C for 2 h. The strength decreased when they were exposed to 650 °C for 1 h, but it increased following a treatment temperature of 825 °C. An exposure temperature of 650 °C appeared to be the level that marks the highest rate of strength reduction. Addition of 20% perlite caused a substantial decrease in the tensile strength of the bricks at all of the exposure temperature investigated. Depending on the price of the perlite, the required thermal conductivity and the acceptable tensile strength, the perlite content of the bricks can be adjusted.

4. Conclusion

The results of this investigation revealed that it was possible to produce lightweight, heat-insulating, water-resistant bricks from pumice and/or perlite without using cement and/or plaster binder. The highest tensile strength was achieved when molasses binder containing 2.5% NH_4NO_3 hardener and 2.5% borax was added into the composition of the bricks. Without the addition of 2.5% borax into the bricks, the H_3PO_4-hardened molasses-bonded bricks should be preferred because their tensile strengths were higher at high-heat treatment temperatures. Depending on the thermal conductivity and density required from the bricks, the replacement ratio of perlite with pumice in bricks can be adjusted, but a substantial reduction in the tensile strength of the bricks may result.

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