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Fabrication of porous anorthite ceramics using eggshell waste as a calcium source and expanded polystyrene granules

Kalsiyum kaynağı olarak yumurta kabuğu atığı ve genleştirilmiş polistiren granülleri kullanılarak gözenekli anortit seramik üretimi

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Fabrication of Porous Anorthite Ceramics Using Eggshell Waste as a Calcium Source and Expanded Polystyrene Granules

Highlights

- *Utilization of eggshell waste and EPS granules in porous anorthite ceramic production*
- *Determination of optimum additive rates and production temperatures*
- *Investigation of the physical and mechanical properties of the ceramics produced*

Graphical Abstract

Highly porous and lightweight ceramics were successfully produced from the admixtures of fireclay as a source of SiO_2 and Al_2O_3 and eggshell waste as a source of CaO in compositions suitable for anorthite production alongside EPS as a pore-forming material.

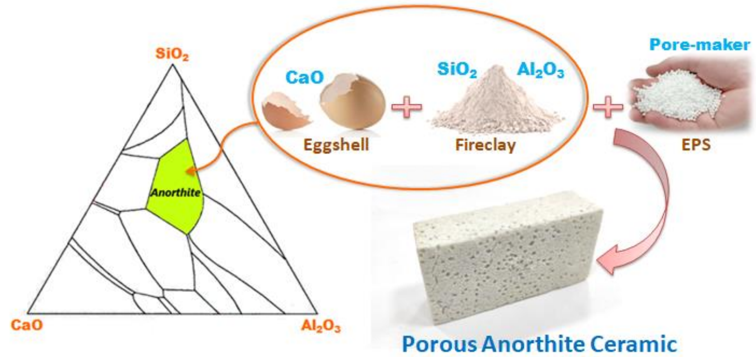

Figure 1. Graphical abstract of the study

Aim

The aim of this study is to produce porous anorthite ceramics by using eggshell waste, an alternative calcium source, and fireclay and pore-forming expanded polystyrene.

Design & Methodology

Phase analysis, microstructural properties, thermal conductivity, density and compression strength values of anorthite samples produced according to the determined optimum additive ratios and sintering temperatures were characterized.

Originality

Although there are numerous studies on the production of porous anorthite ceramics using various raw materials, no study has yet been reported in the literature in which eggshell waste is used in the production of anorthite-based lightweight materials.

Findings

It was concluded that the eggshell waste could be used as a favorable alternative calcium source for the production of porous anorthite ceramics due to their organic and inorganic content.

Conclusion

The thermal properties of the produced anorthite ceramics decreased by 71.8%, as expected, with a 20% reduction in density. Due to the increasing amount of pores, a remarkable decrease of 54.7% in compressive strength occurred.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Fabrication of Porous Anorthite Ceramics Using Eggshell Waste as a Calcium Source and Expanded Polystyrene Granules

Araştırma Makalesi / Research Article

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ABSTRACT

Within the scope of present work, porous and lightweight anorthite ceramics by utilizing admixtures of eggshell waste, fireclay, and expanded polystyrene (EPS) addition has been produced. First, samples of mixtures prepared with different proportions of eggshell waste were fired at different temperatures in order to determine the appropriate anorthite composition. Later, in order to produce high porosity anorthite ceramics, different amounts of EPS are added to the most suitable composition determined and porous samples were produced by firing at the certain temperature. The high degree of porous anorthite ceramics from the admixtures in the range of 0 to 30 vol.% EPS addition were satisfactorily fabricated. The physical characteristics, compressive strength and thermal conductivity were examined. Thermal conductivity of the anorthite ceramics showed a decline from 0.39 W/m·K (1.00 g/cm^3) to 0.11 W/m·K (0.78 g/cm^3) in proportion to the decrease in density. It has been found from the results in which these porous materials produced by the reuse of eggshell waste are suitable for use in various applications requiring elevated temperatures.

Keywords: Anorthite, lightweight ceramics, eggshell wastes, porosity, thermal conductivity.

Kalsiyum Kaynağı Olarak Yumurta Kabuğu Atığı ve Genleştirilmiş Polistiren Granülleri Kullanılarak Gözenekli Anortit Seramik Üretimi

ÖZ

Mevcut çalışma kapsamında yumurta kabuğu atığı, ateş tuğlası ve genleştirilmiş polistiren (EPS) karışımları kullanılarak gözenekli ve hafif anortit seramikler üretilmiştir. İlk olarak, farklı oranlarda yumurta kabuğu atığı ile hazırlanan karışım numuneleri, uygun anortit bileşimini belirlemek için farklı sıcaklıklarda pişirilmiştir. Yüksek oranda gözenekli anortit seramikler üretmek için belirlenen en uygun bileşime, farklı miktarlarda EPS ilavesi yapılmıştır ve belirli sıcaklıkta pişirilerek gözenekli numuneler üretilmiştir. Hacimce %0-%30 aralığında EPS ilavesi ile elde edilen karışımlardan başarılı bir şekilde yüksek gözenekli anortit seramikler üretilmiştir. Fiziksel özellikleri, basınç dayanımı ve ısıl iletkenlik değerleri incelenmiştir. Anortit seramiklerin termal iletkenliği yoğunluktaki azalmayla orantılı olarak 0,39 W/m·K (1,00 g/cm^3)'den 0,11 W/m·K (0,78 g/cm^3)'e bir azalma göstermiştir. Elde edilen sonuçlara göre, yumurta kabuğu atıklarının yeniden kullanılmasıyla üretilen gözenekli anortit seramiklerinin, yüksek sıcaklıklar gerektiren uygulamalarda kullanıma uygun olduğu bulunmuştur.

Anahtar Kelimeler: Anortit, hafif seramikler, yumurta kabuğu atığı, porozite, termal iletkenlik.

1. INTRODUCTION

Lightweight insulation firebricks (IFBs) are among the most commonly used highly porous refractory groups thanks to their success in thermal insulation and high temperature resistance in industrial applications [1,2]. ASTM divides IFBs into groups expressing service temperatures in Fahrenheit according to the C155 standard. For example, the group 23 represents firebricks with a maximum service temperature of 2300°F (equal to 1260°C), one of which is ceramic materials with anorthite composition. IFBs are widely used in high temperature insulation applications owing to their high porosity between 45% and 90% [3]. These porous materials contain air trapped in their pores, and the trapped air prevents heat conduction. The amount of air trapped in the pores in the material increases and therefore the thermal conductivity of the material decreases. It is usual to increase material porosity to achieve lower thermal conductivity. Li et al. stated that the relationship between the amount of pore and thermal conductivity has been studied inclusively and several

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analytical models have been suggested to explain this effect [4]. However, thermal conductivity relies not only on the amount of pore but also on factors such as the size and shape of the pore, chemical and mineralogical composition [1,5,6].

In porous ceramics, the controlled microstructure can be created by incorporating pore forming agents into the system and using different methods. Various processing techniques can be used to fabricate porous ceramics such as gel casting [7–9], freeze-drying method [10–12], direct foaming [13] and sacrificial templates method [14]. Alongside the existing methods, the use of pore-forming agents that burn during firing is most common for IFBs production. In this method, sawdust, rice husk, fine coke, starch, wheat particles, expanded perlite and vermiculite or high-molecular synthetic compounds such as foam polystyrene, polyethylene, polyvinyl are added as flammable materials to form a pore during firing [5,6,14–20].

Until now, many research studies have been carried out on anorthite-based ceramics. Anorthite ceramics can be grouped as dense and porous ceramics according to their usage fields and their engineering properties. Thanks to its outstanding physical properties such as low thermal expansion coefficient, low dielectric constant at high frequencies, and excellent thermal shock resistance, these materials with dense structures are used in low temperature co-fired ceramic surface applications, electrical insulators, and electronic devices for mobile communications [2,21–25].

Cheng et al. also reported that anorthite ceramics can be used in tableware porcelains to increase service and quality thanks to its low relative refractive index [24]. Capoglu et al. carried out various studies to produce anorthite based on whiteware and porcelainised stoneware materials [26–28]. In addition to these, Agathopoulo et al. reported that the fluorapatite-anorthite binary system is a promising material that can be used in biomedical materials [29].

Porous anorthite based IFBs have been the focus of interest in their use as thermal insulators thanks to their high melting point, low theoretical density, low thermal conductivity and low thermal expansion coefficient [2,4,30,31]. These materials can be produced synthetically cheaply from various raw materials. Until now, raw materials such as calcite, quartz, kaolinite, alumina have been the most frequently used materials in investigations on anorthite ceramic production [1,31]. However, in recent years, there has been also significant research on the reuse of waste materials as a new source of raw material [1,2,32–35]. Solid wastes-based porous ceramics have fascinated more and more relevancies because of their environmentally friendly and low-cost on the extensive usage of solid wastes [36]. By this time, many studies have been carried out on calcium-based alternative raw materials for CaO, one of the main components of anorthite. A patent was added to the literature by Brosnan on the usage of recycled paper waste in the manufacturing of low density ceramics [32]. Sutcu et al. generated a sort of porous anorthite ceramic from recycled paper processing residues and clay of diverse sources at 1200-1400°C and stated that using recycled paper waste can be utilized as a convenient option raw material source to fabricate porous anorthite ceramics under favour of its organic and inorganic ingredient [1,2]. The filter cake, a by-product in the sugar beet industry, was used by El-Maghraby et al to obtain anorthite as an alternative source of calcium. They reported that anorthite could be attained as a predominant phase over 1200°C up to 1350°C [33]. Lime sludge is a product that occurs during the causticisation step in the paper production process. Qui et al. was managed to produce anorthite at 1000°C using lime sludge and fly ash released during the alkali recycling process [34]. They have produced anorthite ceramic using a beneficial alternative to contribute to waste recycling. Using steel slag wastes and high alumina containing fly ash as the main raw material, Zong et al. has synthesized porous anorthite ceramic with a porosity of about 49% at a low temperature of 1170°C. Their work provided a new idea for the use of high alumina fly ash [35].

Evaluated as the 15th largest food industry pollution by the Environmental Protection Agency, eggshell waste is actually a quite substantial resource for calcium based ceramic compositions. When the eggshell is subjected to heat treatment at just about 900°C, it includes over 99% CaO by weight. For this reason, it has the potential to be used in many different products from food products to industrial application products as a source of calcium [37,38]. Vichaphund et al. synthesized the single-phase wollastonite at 1100°C utilizing the admixture of bio-solid waste eggshell and silica by microwave-assisted solid-state reaction [39]. Finally, the low thermal conductivity values of 0.25-0.29 W/m·K led them to conclude that calcium silicate produced by adding eggshell waste can easily be used as a thermal insulation material [40].

Although there are numerous studies on the fabrication of porous anorthite ceramics using various raw materials, no study has yet been reported in the literature in which eggshell waste is used for the production of anorthite-based lightweight materials. To cope with, eggshell wastes and fireclay with pore making polymer additives were utilized so as to fabricate porous anorthite insulating firebricks. Adding eggshell waste, an alternative source of CaO to the calcium silicate system, allows us to create an anorthite composition. During firing, the combustion of pore-maker expanded polystyrene (EPS) and the decomposition of calcium carbonate ($CaCO_3$) contribute to occur a more porous structure by creating micro and macro-sized gaps in the body.

2. EXPERIMENTAL PROCEDURE

In this study, commercially purchased fireclay (chamotte125, Esan, Turkey) as a source of alumina (Al_2O_3) and silica (SiO_2) and eggshell waste collected from catering companies as a source of calcium was used for the production of porous anorthite ceramics. This waste also has a pore-making effect due to the degradation of calcium carbonate in the course of firing. Collected eggshells were exposed to pretreatments such as rinsed with distilled water, drying at 50°C overnight, and then grinding in mechanical disc milling to get powder form. Before starting any processing, the physical and chemical features of the raw materials were characterized in advance. Mixtures consisting of fireclay and different ratios of powder eggshell waste (between 20 and 40 wt.%) were prepared for the purpose of forming an anorthite composition. The powder mixture was suitably mixed in a mortar. In order to optimize the firing temperature and eggshell percentage, the prepared powder mixes to optimize firing temperature and eggshell percentage were fired at temperatures of 1250, 1300, and 1350°C for 2 hours in an oven (Protherm PLF 16/15). In the two-stages heating regime, it was reached from room temperature to 400°C with 5°C/min in the first stage, subsequently, from this temperature to the dwell temperatures with 10°C/min.

Table 1. Chemical composition of raw materials (wt.%).

Oxides	Fireclay	Eggshell
SiO_2	57.7	1.25
Al_2O_3	39.6	0.52
Fe_2O_3	0.52	0.10
TiO_2	0.92	-
CaO	0.04	97.1
MgO	0.21	0.56
Na_2O	0.10	0.09
K_2O	0.36	0.11
P_2O_5	-	0.25

microstructural properties of the fired samples were investigated. Density and apparent porosity measurements of each sample were measured by water sinking the sample in accordance with the ASTM C20 standard [41]. Also the weight, dimensional measurements and bulk density of the samples were made by ASTM C134 method [42]. Thermal conductivity analysis of the samples was carried out at room temperature (~30°) using the C-Therm TCi thermal conductivity analyzer. Compressive strengths were tested with a mechanical test machine with a loading speed of 1mm/min. Crystalline phases of the samples were investigated by XRD analysis (Bruker D2 Phaser) using Cu-Kα radiation. Microstructures of fired samples were monitored through scanning electron microscope (SEM).

3. RESULTS and DISCUSSION

3.1. Characterization of Raw Materials

The chemical compositions of commercially purchased fireclay with a powder size under 75μm and the eggshell waste collected from household kitchens and grinded to sizes below 100μm are shown in Table 1. Composed of a high percentage of alumina and silica, fireclay consisted of a low percentage of sodium, potassium, and calcium. The eggshell is composed of mainly calcium oxide.

The XRD patterns of the raw materials were depicted in Fig. 1. The raw eggshell waste (Fig. 1a) is comprised actually of calcite ($CaCO_3$). The crystalline phases determined within raw fireclay material (Fig. 1b) were quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), and cristobalite (SiO_2). Since fireclay is a thermally processed vitrified clay, the loss on ignition is close to zero. Fireclay demonstrates characteristic large humps near crystalline peaks. This is due to the melting alkali forming an amorphous structure during the heat treatment of fireclay.

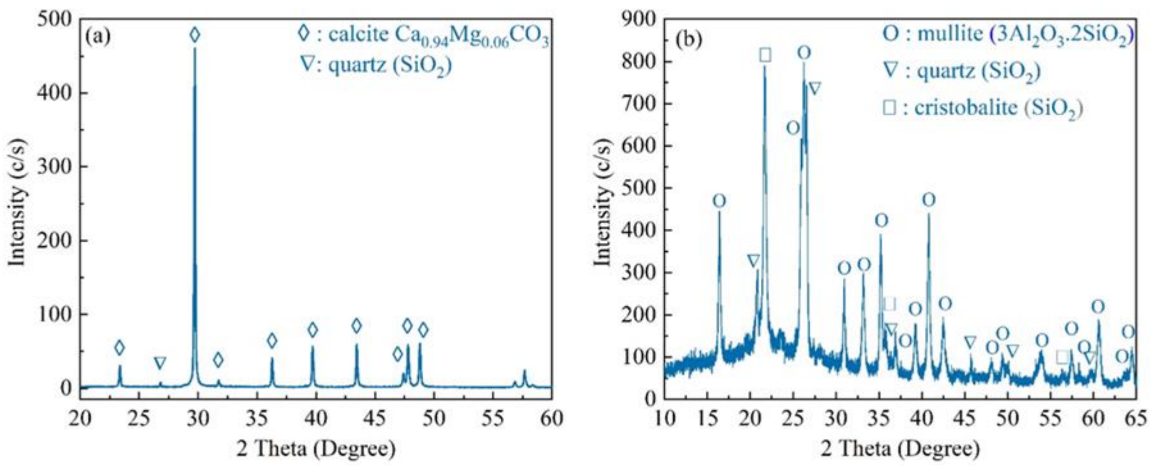

Figure 1. XRD patterns of raw eggshell waste (a) and fireclay (b).

The physical properties obtained from Archimedes' method, thermal conductivity, compressive strength, and TGA/DTG curves that showed the thermal behavior of the eggshell waste sample are in Fig. 2. The results show

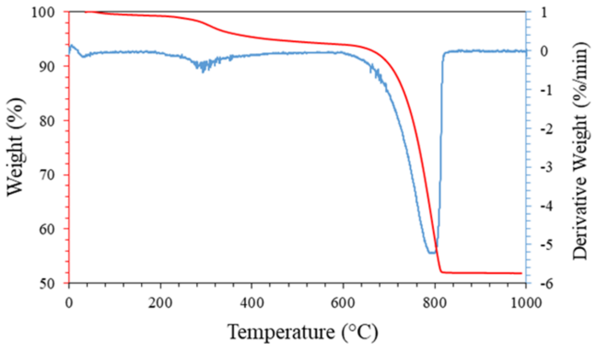

Figure 2. TGA curves of eggshell waste

that the release of physisorbed H_2O, and the organic substances decomposition occurred between 200 and 400°C with a weight loss of 5%. Full calcination occurred at temperatures between 600–840°C with a weight loss of 43%, resulting in phase change owing to the decomposition of $CaCO_3$ to CO_2. The total weight loss of the eggshell was observed as 48% from room temperature to 1000°C.

3.2. Characterization of Fired Samples

Mixtures being made up of fireclay and eggshell waste with different proportions (20–40 wt.%) were fired at several temperatures including 1250°C, 1300°C, and 1350°C for the purpose of finding the optimum conditions of anorthite composition. XRD patterns of fired samples involving the admixtures of fire clay and eggshell waste are shown Fig. 3. Since a high amount of anorthite phase and less amount of mullite phase were observed in XRD patterns, optimum conditions for production of anorthite were determined as 1300°C temperature and 35 wt.% eggshell addition. The photographs of porous anorthite samples with EPS addition in different proportions (0-30 % by volume) are shown in Fig. 4. The macro-pores that formed on the surfaces of the samples after firing are obviously observed due to burning of fine EPS granules.

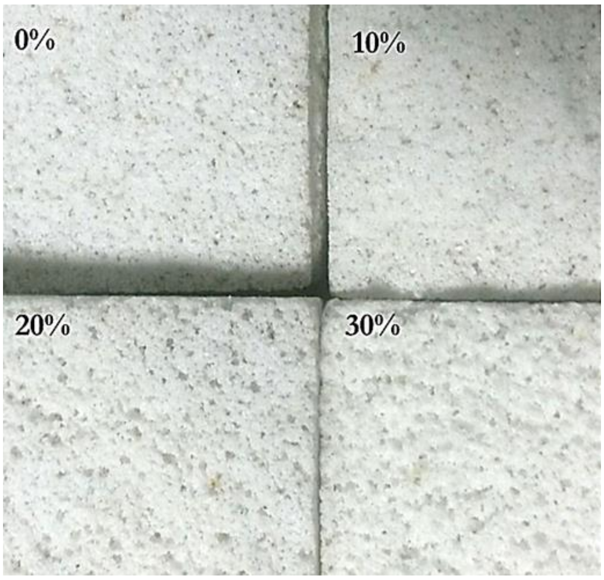

Figure 4. Photographs of the porous anorthite ceramics with EPS addition.

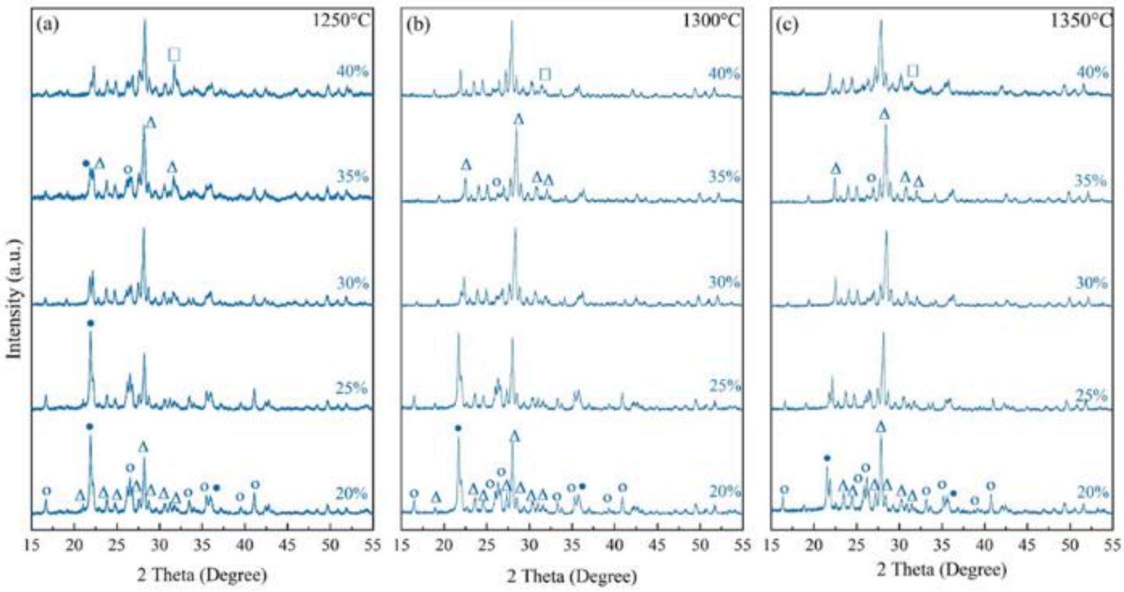

Fig 3. XRD patterns of the ceramic samples with eggshell addition fired a) at 1250°C, b) at 1300°C, c) at 1350°C (o: mullite, Δ: anorthite, •: cristobalite, □: gehlenite).

The physical properties, thermal conductivity, and the compressive strength of the anorthite ceramics produced in the present study were measured. Experimental results of anorthite samples with EPS additive in different proportions (0-30 % by volume) are listed in Table 2. The apparent porosity of the fired samples varied between 61% and 68.1%, with the addition of EPS.

Table 2. Test results of porous anorthite samples fired at 1300°C.

	EPS addition (ratio by volume)			
Physical properties	**0%**	**10%**	**20%**	**30%**
Apparent porosity, %	61±0.1	63±0.2	66.1±0.9	68.1±1.2
Water absorption, %	57.6±0.1	62.4±0.3	72.5±0.6	79.7±0.7
Apparent specific gravity, gr/cm^3	2.72±0.02	2.74±0.01	2.69±0.05	2.68±0.04
Bulk density, gr/cm^3	1.06±0.02	1.01±0.02	0.91±0.04	0.86±0.06
Bulk density, gr/cm^3 (ASTM C134) [42]	1.00±0.04	0.97±0.02	0.85±0.05	0.78±0.03
Thermal conductivity, W/m·K	0.39±0.01	0.32±0.02	0.22±0.02	0.11±0.03
Compressive strength, MPa	6.4±0.9	3.95±0.2	3.8±0.2	2.9±0.4

Thermal conductivity and bulk density of samples with 0% and 30% EPS additive exhibited decreases of 71.8% and 18.9%, respectively. As the bulk density decreased, the thermal conductivity also decreased. Meanwhile the lowest bulk density was 0.86 g/cm^3, thermal conductivity values of and 0.11 W/m·K in samples with 30% EPS that were fired at 1300°C. In addition, the bulk density of samples from weight and dimensional measurements were calculated between 1.00 g/cm^3 and 0.78 g/cm^3 according to EPS addition. From these results, it is noteworthy that the physical properties of the samples containing 30% EPS are consonant with the group 23 IFBs [3]. The compressive strengths of the produced samples exhibited decreasing with increasing EPS ratios. In addition to the decomposition of calcium carbonate, the addition of EPS increased the number of pores in the structure and caused a decrease in density and conductivity values. The presence of a high amount of pores in the structure caused a significant change in the compressive strength. As can be seen from Table 2, the compressive strength of samples fired at 1300°C and added to a maximum of 30% EPS showed a decrease of about 55%, and the compressive strength was observed 2.9 MPa.

Fig. 5 shows SEM images of anorthite sample produced from mixture of fireclay and 35% eggshell waste. It has been observed that the ceramic samples have composed of fine-grained crystals with plate like form.

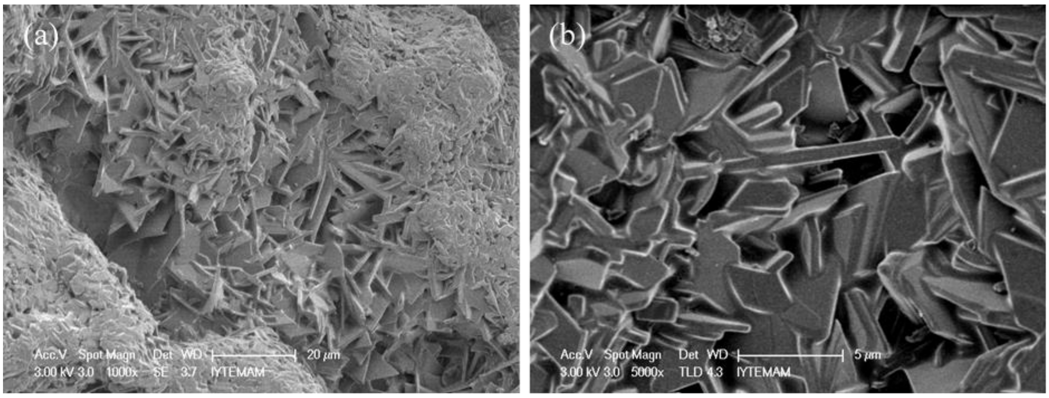

Figure 5. SEM images of anorthite sample with 35% eggshell additive fired at 1300°C: (a) 1000x, (b) 5000x.

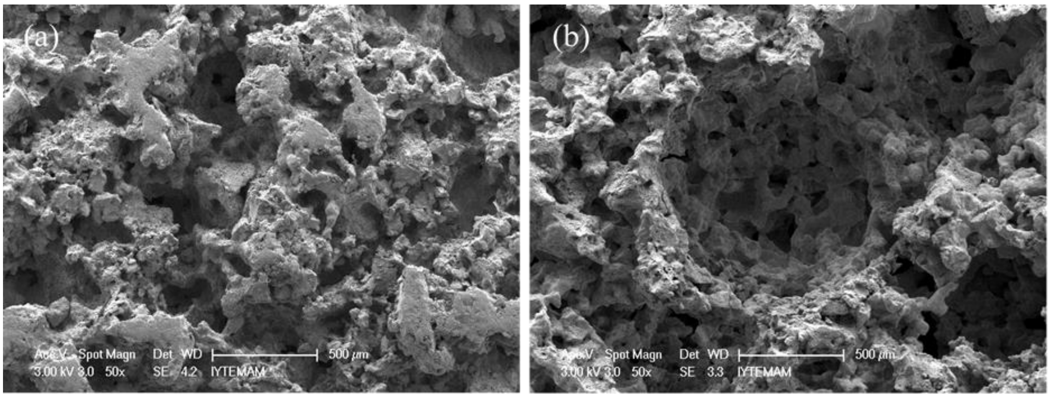

Figure 6. SEM images of the fired anorthite samples with 35% eggshell additive at 1300°C according to EPS addition of (a) 0%, (b) 20%.

The microstructures of 0% and 20% EPS added anorthite samples fired at 1300°C are shown in Figs 6a and 6b, respectively. SEM micrographs of samples reveal that the effect of EPS addition was clearly seen from the microstructures. Most of the pores occurred as a result of the removal of polystyrene besides the decomposition of $CaCO_3$ throughout firing. Formation of micro and macro pores were observed due to gas output and burning of fine EPS spheres. The formation of a highly porous structure also contributed to lower thermal conductivity.

4. CONCLUSION

In conclusion, we have been able to successfully produced porous anorthite ceramics, for the first time, by using fireclay, eggshell waste, and pore-forming expanded polystyrene. In the examples, it was found that a firing temperature of 1300°C and an eggshell additive of 35% would be well enough to fabricate a porous anorthite ceramic. All of the samples included anorthite as the main phase and mullite as the minor secondary phase. The physical properties of the anorthite samples obtained after adding EPS at different rates (0-30%) to the mixture to increase porosity were investigated. It was deduced that bulk densities varied from 1.00 to 0.78 g/cm^3, and also thermal conductivities ranged from 0.39 to 0.11 W/m·K relying on the amount of porosity. Increasing the porosity in the structure led to a decrease in bulk density and thermal conductivity, thus increasing thermal insulation. This situation is the same for compressive strength. With the increase in porosity, the compressive strength of the samples changed between 6.4 and 2.9 MPa.

Finally, it was concluded that the eggshell waste could be utilized as a favorable alternative calcium source for fabrication of porous anorthite ceramics thanks to organic and inorganic content. It can contribute to further this work use various waste calcium sources to support recycling, and produce a more porous structure in order to obtain better results from thermal conductivity tests.

DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Merve TORMAN KAYALAR: Wrote the manuscript.

Gökhan ERDOĞAN: Performed the experiments and analysed the results.

Ahmet YAVAŞ: Supported the writing and editing of the article.

Saadet GÜLER: Supported the writing and editing of the article.

Mücahit SÜTÇÜ: Analysed the results. Guided the article writing process and checked the entire article before submitting it.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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