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# Effect of Calcium Stearate on the Thermal Conductivity of Geopolymer Foam

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**Abstract:** Geopolymers are considered an alternative to conventional cement recently. The use of fly ash and blast furnace slag in geopolymer, which are waste products considered as an environmentally friendly product due to the solution to the storage of wastes also. Geopolymer concrete production is also reported to be 44-64% less than the cement that causes the most $CO_2$ emissions. $CO_2$ emissions are reduced due to the minimum processed natural minerals and industrial waste products used in the geopolymer system. For this reason, this study comes to the fore in terms of the evaluation of wastes. Production of porous geopolymers is potential in use in many industrial applications such as filtering, thermal insulation, light structural material, and catalysis. By controlling the pore type, pore size distribution, pore connectivity, and shape of porosities, potential usages are differentiated. In this study, closed porosity geopolymer foams were produced by the geopolymerization technique with the help of hydrogen peroxide and calcium stearate (CaS) as a surfactant. The thermal conductivity, density, and strength values was correlated with the changing pore size distribution depending on the amount of surfactant and foaming agent. In this study, porous geopolymers with density values 450-500 $kg/m^3$, 0.069 W/mK thermal conductivity, and 2.1 MPa strength value was reached. The reduction in pore sizes due to CaS increase was analyzed. However, we did not observe a decrease in thermal conductivity values due to the reduction of the pore size. Exciting results for CaS content on thermal conductivity were reported.

**Keywords:** Calcium stearate, foam, geopolymer, porosity, thermal conductivity.

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## INTRODUCTION

An incredible acceleration is seen in the construction sector in recent years, and the necessity of the technically superior parameters and values of the construction materials to be used pave the way for the use and application of many new construction materials. Significantly, the sustainability concept that arises due to the rapid consumption of fossil energy resources, air pollution caused by greenhouse gas, the effort to minimize the amount of energy use, and the lack of proper use of the produced materials accelerates the research and development of these materials (1–3).

Today, in parallel to the increasing environmental awareness, national and international environmental policies are becoming more stringent. Kyoto Protocol has been signed by many countries, and studies have been started to reduce $CO_2$ emissions. The World Business Council for

Sustainable Development says it is responsible for the cement sector for about 5% of $CO_2$ emission. It is an indication that the cement sector has a significant impact on the increase in $CO_2$ emissions. (4). The concrete and cement sector has been criticized for not only high emissions of carbon dioxide but also consuming large amounts of natural resources and energy mainly from cement production. These justified criticisms are tried to be overcome by alternative solutions. With the addition of fly ash, industrial waste in cement-based systems (such as plaster, mortar, concrete) can be minimized, and carbon dioxide emission can be minimized, and the need for natural resources is reduced (5–12).

In our country, resources such as petroleum, coal, and natural gas are used for energy production. As presented in TÜIK 2015 and 2016 reports, coal use for energy production is expected to increase gradually by 2040 (13,14). It means that by-products such as fly ash and bottom ash formed as a result of the combustion of coal will also increase gradually. While Japan recycled 96% of fly ash in the context of cyclic economy and England, India, America, Australia recycles about 50% of the fly ash; this ratio remains 15% in Turkey (14). One of the other objectives of this study is the fact that the fly ash, which is generated as a waste of millions of tons per year, can be converted into added-value products.

Secondly, energy efficiency in buildings is always an important issue. Demand for energy, which is indispensable for human life, is increasing rapidly with population growth, industrialization, and urbanization. Meeting the increasing energy consumption in the world where there is limited energy supply has been a problem for many countries, and the dependence on foreign energy has increased (15). In Turkey, a large part of the energy consumption consists of housing under the name of city consumption. Heat insulation is one of the most critical measures that can be taken to ensure energy efficiency in houses.

Thermal insulation materials used in buildings are the most effective solution in reducing heat losses. In this way, it contributes to the almost zero energy target by reducing the heat energy requirement in buildings. It is necessary to produce a foam geopolymer with homogeneously distributed and closed porosity to provide thermal isolation (16,17).

Many articles on porous geopolymer production have been published. In the direct foaming method, which is the most commonly used method, foam materials are produced by adding gas-forming additives to a suspension or liquid medium. Foaming is usually done by adding $H_2O_2$, Al powder, metallic Si, and sodium perborate as a foaming agent to the geopolymeric mixture and mixing them mechanically. After the decomposition of additives in an alkaline slurry, a bubble forms and a porous structure is formed (7,18–21). Besides, the amount of porosity, which depends on the amount of foaming agent used, also depends on whether the foams can remain stable in the mixture. Additives are needed to ensure that thermodynamically unstable gas bubbles are kept in the mixture and are homogeneously distributed. These additives are referred to as surfactants. Many studies have been conducted on butyric acid, valeric acid, butyl gallate, propyl gallate, hexylamine, oleic acid, and albumin as surfactants in foam geopolymer production (22–31). However, there are only limited numbers of publications on CaS, and its effect on the thermal conductivity properties. Cui et al. reached a minimum thermal conductivity value of 0.096W / mK from their work, depending on the amount of CaS. They observed that although samples containing a fixed amount of stearate reached a minimum value of 0.048W/mK by changing the water/binder amount, this negatively affected the mechanical properties (24,32).

This study was carried out on the development of porous geopolymer wall elements for insulation with the help of CaS as a surfactant. This study gains importance in $CO_2$ emission, cyclic economy, and energy fields thanks to the reduction of cement use, recycling of fly ash, and the development of thermally insulated wall elements. In this study, the effect of CaS on thermal conductivity is examined from a different perspective. CaS, which reduces the pore size, negatively affected the thermal insulation feature.

## MATERIALS AND METHODS

The mixed composition of foam geopolymer includes fly ash, metakaolin, sodium hydroxide, sodium silicate, expanded perlite, water, and chopped polypropylene fiber (Table 1). Hydrogen peroxide was used as a foaming agent (%35), and CaS was used to obtain foam stabilization. Fly ash (FA) was taken from the Seyitömer Thermal Power Station, Turkey, and metakaolin was supplied from the Czech Republic. Chemical compositions of metakaolin and fly ash are presented in Table 2.

The principle of homogeneous mixing of solid components and liquid components in separate places was followed. First, the NaOH flakes were completely dissolved in water to obtain a 10M environment and then mixed with sodium silicate solution. Geopolymeric slurry was added by adding an alkaline solution to the mixture of metakaolin, fly ash, exploded perlite, and polypropylene fibers mixed separately. After the geopolymer slurry became homogeneous, foaming agent and surfactant were added and mixed. Finally, a foam mixture was poured into 100x100x100 mm molds and cured at 60°C.

The compressive strength tests were conducted with a compressive testing machine on the samples whose dimensions were 100 × 100 × 100 mm. Compressive strength test was applied.

**Table 1.** Composition of foam geopolymer mixtures.

| Code | Fly Ash(%) | Metakaolin (%) | CaS* (%) | Perlite (%) | Fiber (%) |
|---|---|---|---|---|---|
| 1 | 90 | 10 | 0.15 | 0 | 0.21 |
| 2 | | | | 2 | |
| 2 | | | | 4 | |
| 4 | | | | 8 | |
| 5 | 90 | 10 | 0.45 | 0 | 0.21 |
| 6 | | | | 2 | |
| 7 | | | | 4 | |
| 8 | | | | 8 | |
| 9 | 90 | 10 | 0.75 | 0 | 0.21 |
| 10 | | | | 2 | |
| 11 | | | | 4 | |
| 12 | | | | 8 | |

**Table 2.** Chemical content of Fly ash and Metakaolin.

| | Fly Ash | Metakaolin |
|---|---|---|
| $SiO_2$ | 50.30 | 54.10 |
| $Al_2O_3$ | 19.10 | 41.10 |
| CaO | 4.55 | 0.13 |
| $Fe_2O_3$ | 12.40 | 1.10 |
| MgO | 4.67 | 0.18 |
| $K_2O$ | 2.16 | 0.80 |

After drying, the unmolded samples were stored in the laboratory conditions for 28 days. The thermal conductivity coefficient λ was calculated with a modified transient plane source. The bulk density of the product was calculated as the mass to volume ratio of the sample.

## RESULTS AND DISCUSSION

### Density and Porosity

According to scanning electron microscopy analysis, samples have closed porosity, pore morphology is pretty homogeneous, and pore dimensions are getting smaller following the surfactant amount (Figure 1). Measurements were taken from perlite-free samples. Samples contain 0.15%, 0.45% and 0.75% CaS, respectively. The pore sizes varying depending on the amount of CaS are 928.8 µm, 659.5 µm, and 573.5 µm, respectively. Pore sizes were observed to change inversely proportional to the amount of CaS.

Density was effected directly proportional to the amount of surfactant in the foam geopolymer mixture. Utilizing $H_2O_2$, the gas bubbles formed in the geopolymer slurry were further kept in mixture with the effect of the increased amount of surfactant, and therefore the density decreased. Density values also gradually decreased inversely proportional to the amount of perlite added to the mixture. The lowest density value at different Ca stearate concentrations were obtained in samples containing 8% perlite. The highest density values were also measured in samples without perlite (Figure 2).

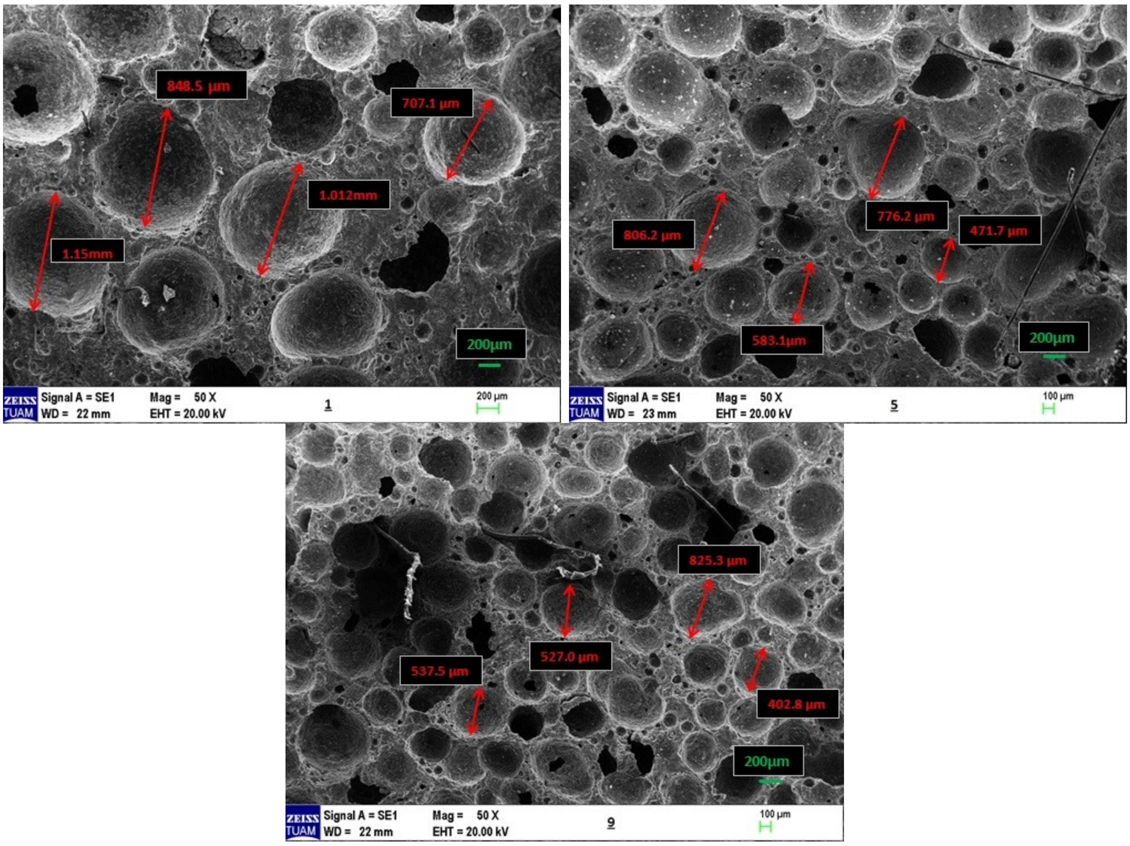

**Figure 1.** Scanning electron microscopy images of geopolymer foams at 50X magnification. Foams contains upper row, left) 0.15%, upper row, right) 0.45%, and lower row, center) 0.75% CaS.

## Compressive Strength

The compressive strength values recorded from an average of three cubic specimens with dimensions of 100×100×100 $mm^3$ cured during 28 days were tested. The results of the compressive strength of geopolymer foams are shown in Figure 3. The perlite-free foams had higher strength values compared to the samples containing 8% perlite. A gradual decrease in compression strength values was observed with the increase of perlite input into the composition. This decrease in compressive strength is due to the lower strength (0.1-0.4MPa) and porosity of perlite (33). It is also due to the highly crushable behavior of expanded perlite during compression (34). Besides, our work suggests that this is because of non-bonding between perlite and geopolymer foam.

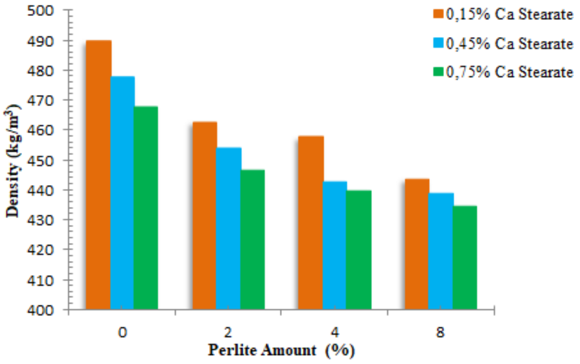

**Figure 2.** Density values of foam geopolymer samples according to perlite amount and CaS concentration.

In the samples without perlite, the strength values changed depending on the amount of CaS. The strength value of the sample without perlite containing 0.75% CaS was 2.14 MPa, while the strength of the sample containing 0.15% CaS was 1.82 MPa.

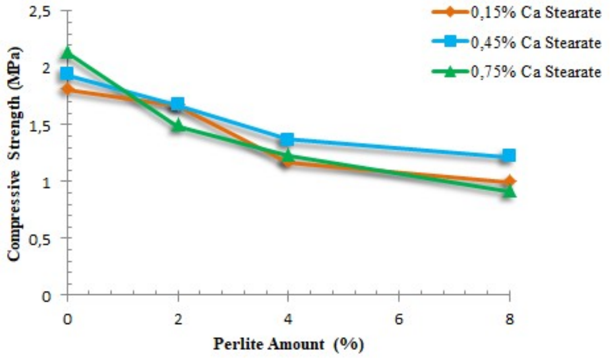

**Figure 3.** Compressive strength values of foam geopolymer samples according to perlite amount and CaS concentration.

### Thermal Conductivity

Figure 4 presents the thermal conductivity performances of geopolymer mixtures. Thermal conductivity tests were carried out on all twelve geopolymer mixtures. It is evident that the perlite input into the mixture gradually reduces the thermal conductivity values for all samples. The minimum thermal conductivity value was obtained at 8% perlite input for all samples.

Considering the amount of CaS, surprising results were obtained when the thermal conductivity values were examined. Considering the Knudsen effect (35,36), thermal conductivity is expected to decrease as the pore size decreases. According to theory, when the pore diameter of the material becomes less than the average free length of the path of gas molecules, the molecules only collide with pore surfaces without transferring energy. Baetans et al. (44) also summarized this statement and said that reducing cell sizes is a very effective way to reduce the thermal conductivity of insulating material. However, an increase was observed in contrast to the theory in thermal conductivity with cell reduction due to the increasing CaS amount. This situation most probably because water repellant property of CaS (45). As a result of this situation, CaS makes it challenging to remove the water in the sample from the sample during drying. **Table 3.** Foam geopolymer studies reported in the literature and the findings of this study.

Table 3. Foam geopolymer studies reported in the literature and the findings of this study.

| ***Aluminosilicate Precursor*** | ***Activator*** | ***Admixture*** | ***Aggregate*** | ***Foaming Agent*** | ***Pore Size*** | ***Strength (MPa)*** | ***Density (kg/ $m^3$)*** | ***Thermal Cond (W/mK)*** | ***Refs*** |
|---|---|---|---|---|---|---|---|---|---|
| Fly Ash | Water Sodium Silicate | - | - | $H_2O_2$ | - | 0.4-1.43 | 270-375 | 0.071-0.092 | (37) |
| Fly Ash Blast Furnace Slag | NaOH Sodium Silicate Distilled Water | - | - | Foaming Agent | - | 3.0-50.0 | 600-1500 | 0.15-0.5 | (38) |
| Fly Ash | NaOH Sodium Silicate Tap Water | - | - | $H_2O_2$ | - | 1.9-3.4 | 400-650 | 0.083-0.127 | (39) |
| Fly Ash Metakaolin | NaOH Sodium Silicate Distilled water | - | - | $H_2O_2$ | - | 0.26-21 | 440-1100 | 0.082-0.227 | (40) |
| Metakaolin Fly Ash | NaOH Sodium Silicate | - | - | $H_2O_2$ | - | 1.23 | 560 | 0.107 | (12) |
| Fly Ash Metakaolin | NaOH Sodium Silicate Distilled Water | - | Construction and demolition waste | $H_2O_2$ | 0.198-31.88 μm | 3.6-11.9 | 1000-1700 | 0.19-0.44 | (41) |
| Fly Ash Blast Furnace Slag | NaOH Sodium Silicate Water | SDS | - | $H_2O_2$ | 0-2mm | 3.2-44.8 | 140-1020 | 0.183-0.646 | (20) |
| Fly Ash Metakaolin | NaOH Sodium Silicate Water | Surfactant | - | Al | - | 0.6-403 | 430-850 | 0.079-0.170 | (42) |
| Fly Ash Metakaolin | NaOH Sodium Silicate Distilled Water | - | - | $H_2O_2$ | 0.57-1.13mm | 0.68-2.23 | 150-300 | 0.0622-0.0852 | (43) |
| Fly Ash | - | Calcium Stearate | - | $H_2O_2$ | 140 -4563 μm | 1.45-1.65 | 310-360 | 0.095-0.139 | (24) |
| FlyAsh-Metakaolin | NaOH Sodium Silicate Water | Calcium Stearate | Expanded Perlite | $H_2O_2$ | 573-928 μm | 0.925-2.14 | 435-490 | 0.069-0.1052 | This work |

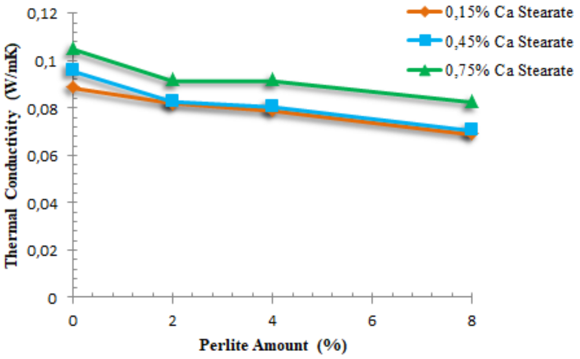

**Figure 4.** Thermal insulation performances of foam geopolymer samples according to CaS and perlite amount.

Table 3 gives the foam geopolymer studies reported in the literature. As mentioned earlier, there are not too many foam geopolymer studies using CaS as a surfactant. Cui et al. obtained the lowest conductivity when using CaS as a surfactant in fly ash based geopolymer foams is 0.096W/ mK (24). Minimum detectable thermal conductivity value among fly ash based foam studies for samples with a density of 150-300kg/ m$^3$, 0.0622W / mK has been reached by Wu et al. (43). The best thermal conductivity value was recorded as 0.069W/mK in a sample containing 0.15% CaS and 8% perlite in this study.

## CONCLUSION

The results show that hydrogen peroxide with CaS is useful in obtaining homogeneous pore morphology with low thermal conductivity. Density was effected directly proportional to the amount of surfactant in the foam geopolymer mixture. Also, the density decline continued with perlite added to the mixture. Although in the construction area, perlite is widely used as an aggregate because of its outstanding insulation characteristics and low weight, it decreases the compressive strength of the foam. The strength value of perlite-free samples increased in direct proportion with the amount of CaS.

An interesting result was encountered in thermal conductivity measurements. Contrary to what the thermal conductivity theorem states, there is no result that thermal conductivity decreases with decreasing pore size. On the contrary, the increased amount of CaS impairs the insulating properties of the sample. This situation was caused by the water repellent feature of CaS. The presence of perlite as an aggregate gave the material better-insulating properties in all samples where thermal conductivity decreased with increasing porous perlite input. The best thermal conductivity value was recorded as 0.069W/mK in a sample containing 0.15% CaS and 8% perlite in this study.

Foamed fly ash geopolymers have good potential in an application for lightweight building materials. These geopolymer mixtures where the amount of perlite is maximum 2% appear to meet the values specified in TSE 13655 (> 1.5MPa, d <450-550kg/ m$^3$ and ʎ <0.12W / mK).

This study shows an environmentalist approach in terms of converting fly ash into value-added products and reducing the use of cement that causes $CO_2$ emission. It supports the protection of the limited energy resources by improving the thermal insulation feature of the walls that have the most energy loss in buildings.

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