

## PERFORMANCE OF FLY ASH-BASED GEOPOLYMER MORTAR

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**Abstract:** *This study has investigated the joint effect of several mix parameters on the properties of foam geopolymers. The mix parameters analysed through a laboratory experiment of 54 different mortar mixes were, sodium silicate/sodium hydroxide mass ratio (2.5, 3.5, 4.5), activator/binder mass ratio (0.6, 0.8, 1.0), chemical foaming agent type (hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and sodium perborate (NaBO<sub>3</sub>)) and foaming agent mass ratio content (1%, 2%, 3%). Properties, SEM and FTIR analysis and cost analysis are included. The results show that the sodium perborate over performs hydrogen peroxide leading to a lower overall thermal conductivity of foam geopolymers. The use of an activator/binder ratio of 0.8 a sodium silicate/sodium hydroxide of 2.5 led to the lowest thermal conductivity. Mixtures with a low thermal conductivity of around 0.1 W/(m.°K) and a compressive strength of around 6 MPa were achieved. The cost analysis show that the foaming agents are responsible for a small percentage of foam geopolymers total cost (less than 10%) being that the alkaline activators are responsible for more than 80%.*

### Introduction

The increasing demand for worldwide energy, is a major cause for the unsustainable development of our Planet. Between 2007 and 2030 energy demand should have grown from about 40% to 16.8 billion tons of equivalent petroleum-TEP [1]. The rise in energy consumption has two main reasons, the increase in world population and the fact that there are an increasing number of people with access to electricity. Currently, 1.5 billion people still have no access to electricity [2]. Besides since urban human population will almost double, increasing from approximately 3.4 billion in 2009 to 6.4 billion in 2050 [3] this will dramatically increase electricity demand. Beyond what energy consumption means in terms of using non-renewable fossil materials, the highest environmental impact of energy consumption, has to do with carbon dioxide emissions, generated during the burning of coal and gas for electricity generation in power stations. Given that buildings consume throughout their life cycle, more than 40% of all energy produced [4], we can easily see the high energy saving potential that this subsector may represent in terms of reducing carbon dioxide emissions. Energy efficiency is the most cost effective way to reduce emissions, improve competitiveness and create employment. The Energy Road Map 2050 [5] confirmed that higher energy efficiency in new and existing buildings is key for the transformation of the EU's energy system. COM 815 [6] mentions that the Union's energy efficiency target of saving 20% of energy by 2020 could cut consumers' bills by up to €1000 per household a year and improving Europe's industrial competitiveness and creating up to 2 million new jobs by 2020. The European Energy

Performance of Buildings Directive 2002/91/EC (EPBD) has been recast in the form of the 2010/31/EU by the European Parliament on 19 May 2010. One of the new aspects of the EPBD that reflects an ambitious agenda on the reduction of the energy consumption is the introduction of the concept of nearly zero-energy building [7]. The use of thermal insulation materials constitutes the most effective way of reducing heat losses in buildings thus reducing heat energy needs. These materials are very important for the building material industry representing a 21 billion € market share [8]. With the exception of expanded cork, which is based on a renewable and completely recyclable material, all the other current insulation materials are associated with negative impacts in terms of toxicity. Polystyrene, for example contains anti-oxidant additives and ignition retardants, additionally, its production involves the generation of benzene and chlorofluorocarbons. On the other hand, polyurethane is obtained from isocyanates, which are widely known for their tragic association with the Bhopal disaster. Besides, they release toxic fumes when subjected to fire [9]. Besides recently the European Union recently approved the Regulation (EU) 305/2011 related to the Construction Products Regulation (CPR) that will replace the current Directive 89/106/CEE, already amended by Directive 1993/68/EEC, known as the Construction Products Directive (CPD). A crucial aspect of the new regulation relates to the information regarding hazardous substances [9]. Investigations in the field of geopolymers had an exponential increase after the research results of Davidovits [10] who developed and patented binders obtained from the alkali-activation of metakaolin, having named it after the term “geopolymer” in 1978. Its worth remembering that the technology of alkali-activation however predates this terminology by several decades [11]. For the chemical designation of the geopolymer Davidovits suggested the name “polysialates”, in which Sialate is an abbreviation for aluminosilicate oxide. The sialate network is composed of tetrahedral anions  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  sharing the oxygen, which need positive ions such as  $(\text{Na}^+, \text{K}^+, \text{Li}^+, \text{Ca}^{++}, \text{Na}^+, \text{Ba}^{++}, \text{NH}_4^+, \text{H}_3\text{O}^+)$  to compensate the electric charge of  $\text{Al}^{3+}$  in tetrahedral coordination (after dehydroxilation the aluminium changes from coordination 6 (octahedral) to coordination 4 (tetrahedral)). Despite all the investigations published on these materials in the last decades some aspects still needed to be further investigated especially concerning durability performance [14-16]. Foam geopolymer constitutes a recent research field with high potential in the development of low toxicity thermal insulators with thermal conductivity value around  $0.22 \text{ W/mK}$  [17-19]. This paper discloses results of a study that has investigated the joint effect of several mix parameters on the properties of foam geopolymers fly ash-based.

## EXPERIMENTAL WORK

Materials, mix design, mortar mixing

The characteristics of the aggregates (coarse and sand) used are shown in Table 1.

Table 1- Characteristics of the aggregates

	Max dimension	Fine content	Density ( $\text{kg/m}^3$ )	Water absorption
Sand	4.0	$\leq 3$	2660	0.2
Coarse aggregates	8.0	$\leq 1.5$	2620	0.6

The fly ash used in the geopolymeric mortars was supplied by Sines-EDP and according to the NP EN 450-1 it belongs to B class and has an N class fineness modulus. Geopolymeric mortars were a mixture of aggregates, fly ash, calcium hydroxide and alkaline silicate solution. A 10% percentage

substitution of fly ash by calcium hydroxide in the mixture was also used. This is because the use of minor calcium hydroxide percentages is pivotal for the strength and durability of geopolymers [15,20]. The sand, fly ash and calcium hydroxide were dry mixed before added to the activator. The alkaline activator was prepared prior to use. An activator with sodium silicate solution ( $\text{Na}_2\text{O}=13.5\%$ ,  $\text{SiO}_2=58.7\%$ , and  $\text{water}=45.2\%$ ) and sodium hydroxide was used. The alkaline activator was prepared prior to use. An activator with sodium silicate solution ( $\text{Na}_2\text{O}=13.5\%$ ,  $\text{SiO}_2=58.7\%$ , and  $\text{water}=45.2\%$ ) and 12 M sodium hydroxide was used. Two chemical foaming agents (hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and sodium perborate ( $\text{NaBO}_3$ )) were used. The mix parameters analysed through a laboratory experiment of 54 different mortar mixes were, sodium silicate/sodium hydroxide mass ratio (2.5, 3.5, 4.5), activator/binder mass ratio (0.6, 0.8, 1.0), chemical foaming agent type (hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and sodium perborate ( $\text{NaBO}_3$ )) and foaming agent mass ratio content (1%, 2%, 3%). The fresh mortar were cast and allowed to set at room temperature for 24h before being removed from the moulds and kept at room temperature (20 °C) until tested. Bulk density was assessed according to the ASTM C 373-78.

#### Experimental procedures

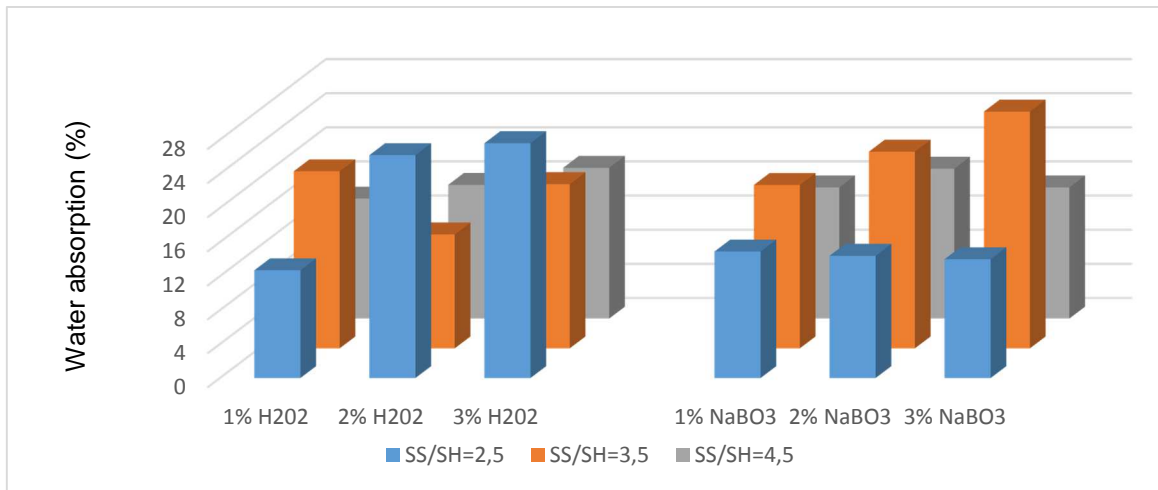
Compressive strength were performed on  $50\times 50\times 50\text{ mm}^3$  concrete specimens according to NP EN 195-1. Compressive strength for each mixture was obtained from an average of 3 cubic specimens determined at the age of 28 days of curing. Water absorption by immersion was performed on  $40\times 40\times 80\text{ mm}^3$  specimens. Specimens were tested with 28 days curing. The specimens were immersed in water at room temperature for 24 hours. First the weight of the specimens while suspended by a thin wire and completely submerged in water is recorded as  $W_{im}$  (immersed weight). After that the specimens were removed from water, and placed for 1 min on a wire mesh allowing water to drain, then visible surface water is removed with a damp cloth and weight is recorded as  $W_{sat}$  (saturated weight). All specimens were placed in a ventilated oven at 105 °C for not less than 24 hours and allowing that two successive weightings at intervals of 2 hours show an increment of loss not greater than 0,1% of the last previously determined weight of the specimen. The weight of the dried specimens is recorded as  $W_{dry}$  (oven-dry weight). Thermal conductivity was assessed using an Alambeta instrument developed at the Technical University of Liberec, Czech Republic. During the measurements, the initial temperature of the samples and the base of the Alambeta were kept at 22-24 °C, and the relative humidity was in the range of 55-65%. To investigate the effect of the temperature drop on the thermal properties of the samples, the temperature of the measuring head at first was 10 °C higher than the environmental temperature. During the second set of measurements, the measuring head was 40 °C higher than the base plate.

#### Results and discussion

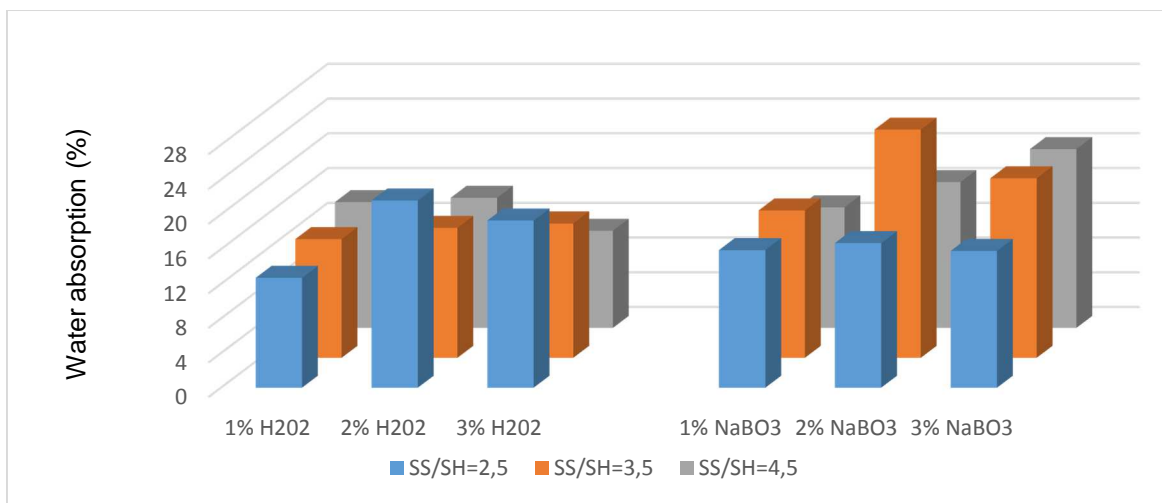
##### Water absorption by immersion

The results of water absorption by immersion are showed in Fig 1. The lowest water absorption by immersion (11.2%) was in a mixture with an activator/binder ratio of 0.8 a sodium silicate/sodium hydroxide of 4.5 and 3% hydrogen peroxide content. Very similar lower water absorption values (12.7%) were found for mixtures with 1% hydrogen peroxide and a sodium silicate/sodium hydroxide of 2.5. One with an activator/binder ratio of 0.8 and the other with an activator/binder ratio of 1.0. The highest water absorption by immersion (27%) were found in a mixture with an activator/binder ratio of 1.0 a sodium silicate/sodium hydroxide of 2.5 and 3% hydrogen peroxide content.

a)



b)



c)

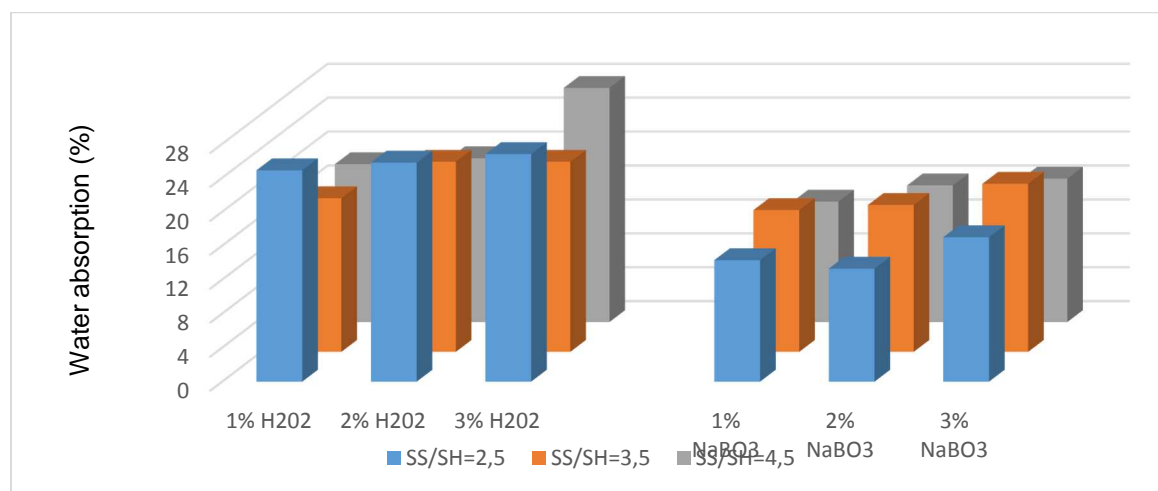
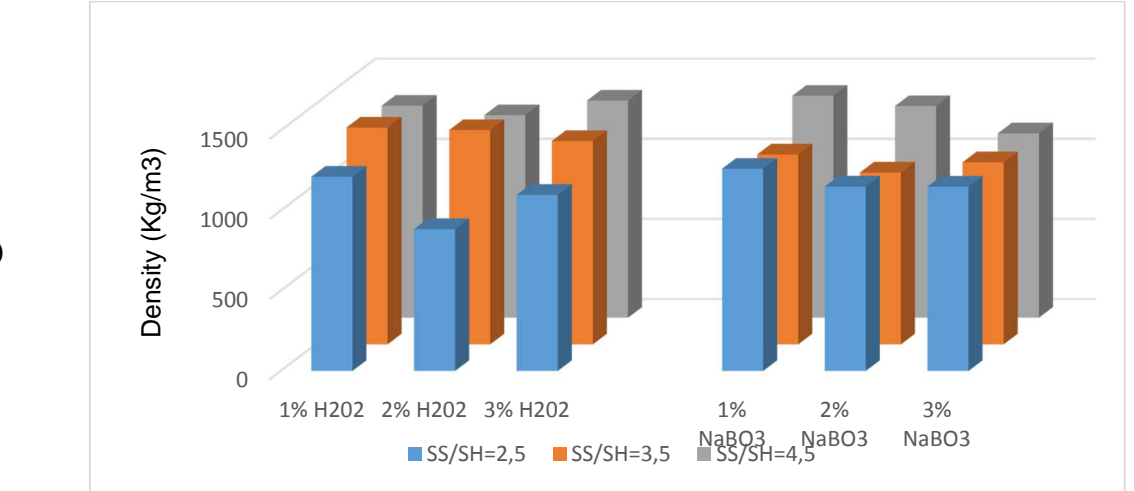
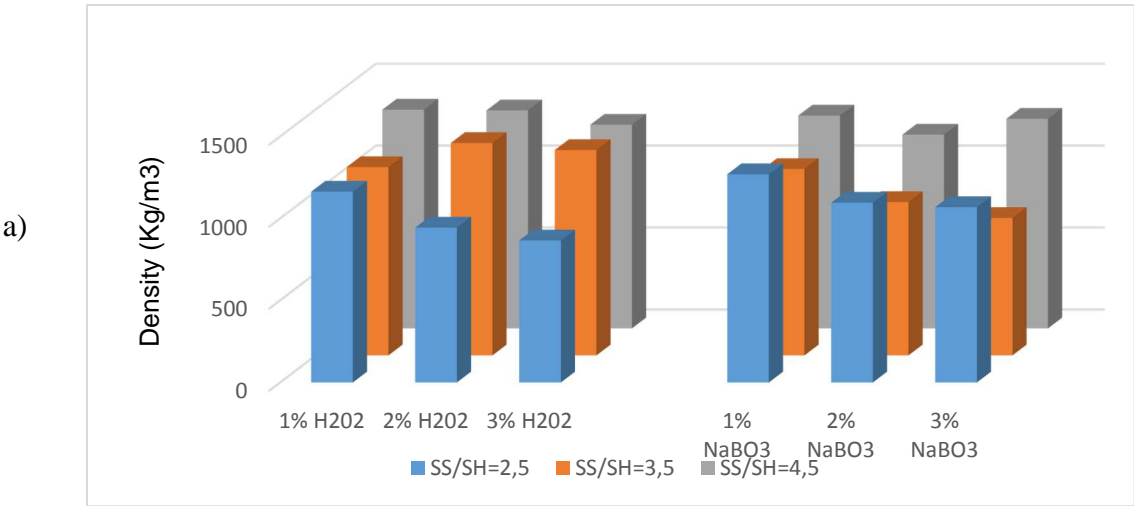


Fig. 1 – Water absorption by immersion according to activator/binder ratio and sodium silicate/sodium hydroxide mass ratio: a) Activator/binder ratio=1; b) Activator/binder ratio=0.8; Activator/binder ratio=0.6

A similar high water absorption (27%) was found in a mixture with an activator/binder ratio of 1.0 a sodium silicate/sodium hydroxide of 3.5 and 3% sodium perborate content and also in a mixture with an activator/binder ratio of 0.6 a sodium silicate/sodium hydroxide of 4.5 and 3% hydrogen peroxide content. This means that concerning water absorption both foaming agents allow for high porosity mixtures depending on the on their content and on the ratios activator/binder and sodium silicate/sodium hydroxide.

Density

The results of density are presented in Fig.2. The lowest density results were found in mixtures with an activator/binder ratio of 0.6 and 3% hydrogen peroxide content. One with a sodium silicate/sodium hydroxide of 4.5 (734 kg/m<sup>3</sup>) and other with a sodium silicate/sodium hydroxide of 2.5 (749 kg/m<sup>3</sup>). As a general trend the increase of foaming agent leads to a lower density. However, the opposite can also take place. That's the case of hydrogen peroxide based mixtures with an activator/binder ratio of 1.0 a sodium silicate/sodium hydroxide of 3.5.



c)

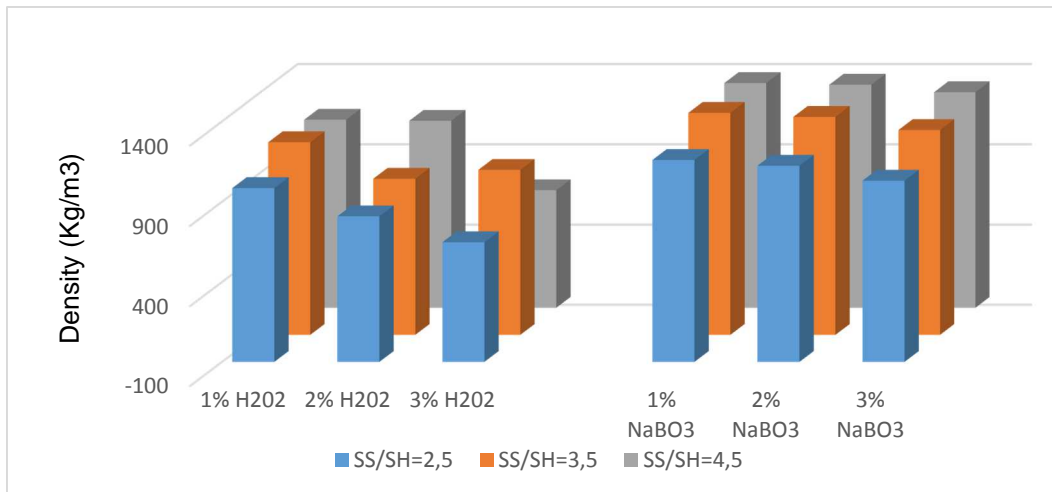
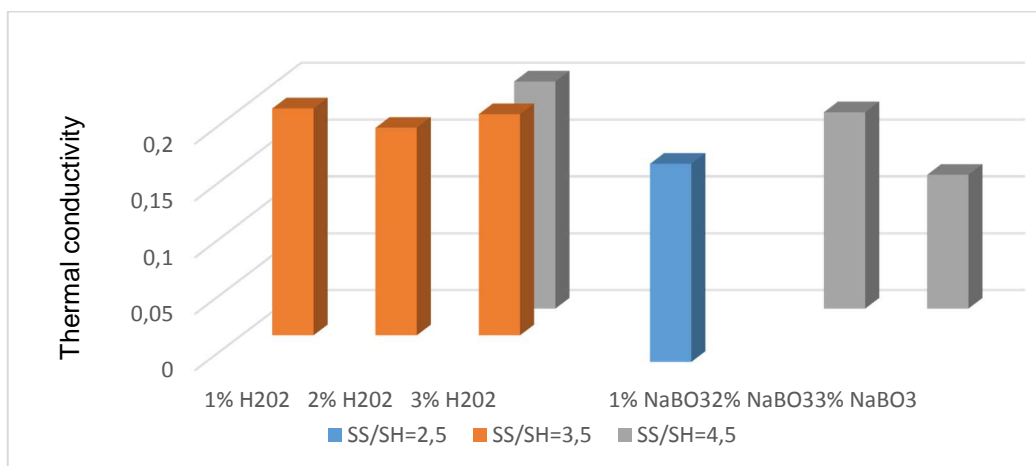


Fig. 2 – Density according to activator/binder ratio and sodium silicate/sodium hydroxide mass ratio: a) Activator/binder ratio=1; b) Activator/binder ratio=0.8; Activator/binder ratio=0.6

#### Thermal conductivity

Figure 3 shows the results of the thermal conductivity. The lowest thermal conductivity performance was achieved (0.113 W/m.°K) in a mixture with an activator/binder ratio of 0.8 a sodium silicate/sodium hydroxide of 2.5 and 3% sodium perborate content. A similar thermal conductivity was obtain in a mixture with the same activator/binder ratio, the same sodium silicate/sodium hydroxide ratio and just 3% sodium perborate content (0.1195 W/m.°K). A mixture with the same sodium silicate/sodium hydroxide of 2.5 with an activator/binder ratio of 0.6 and 2% hydrogen peroxide content also lead to a low thermal conductivity (0.1293 W/m.°K). Another sodium perborate based mixtures with an activator/binder ratio of 1.0 and a sodium silicate/sodium hydroxide of 4.5 also led to a low thermal conductivity (0.1187 W/m.°K). This results outperform the thermal conductivity of commercial autoclaved aerated concrete masonry blocks (Ytong) which are around (0.17 W/m.°K).

a)



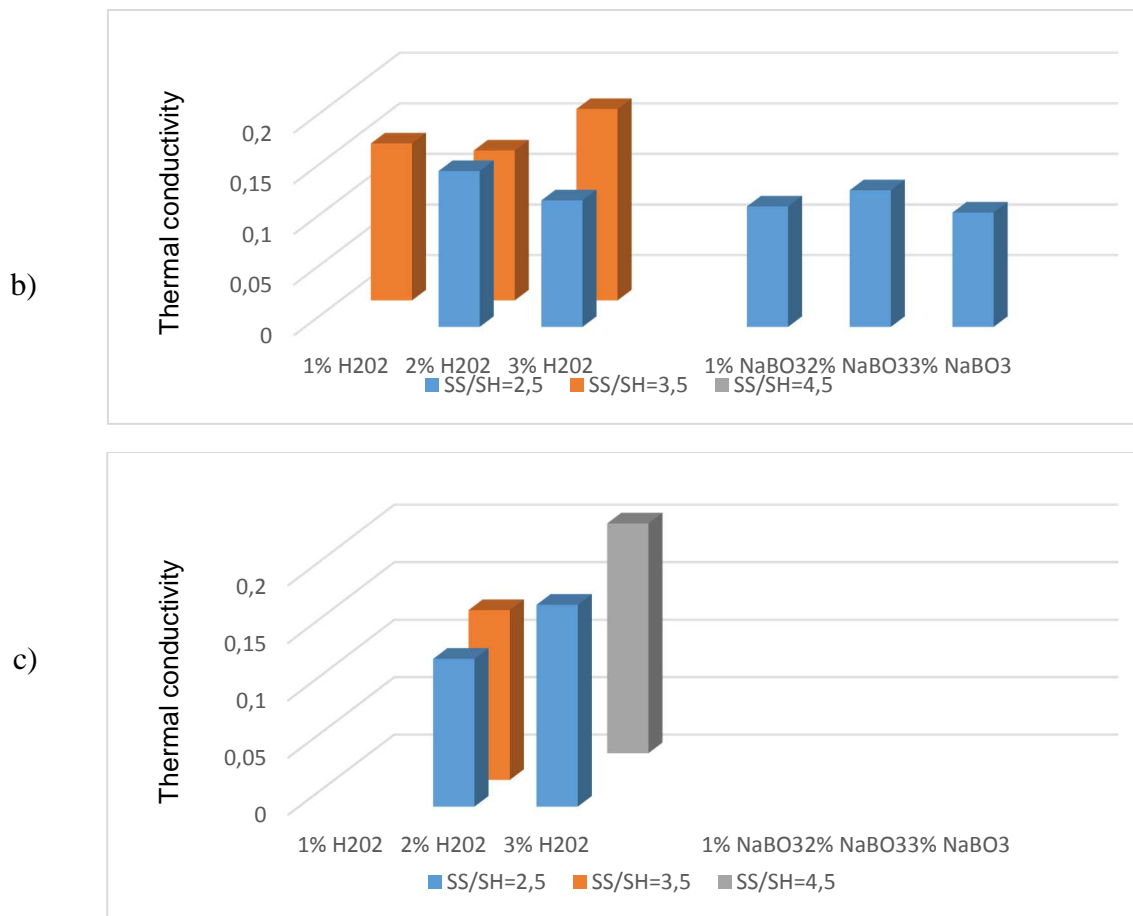


Fig. 3 – Thermal conductivity according to activator/binder ratio and sodium silicate/sodium hydroxide mass ratio: a) Activator/binder ratio=1; b) Activator/binder ratio=0.8; Activator/binder ratio=0.6

### Compressive strength

Fig.4 shows the results of the compressive strength. Low compressive strength results (below 3 MPa) were found in hydrogen peroxide mixtures (2 and 3%) with an activator/binder ratio of 0.8 and a sodium silicate/sodium hydroxide of 2.5. It's important to mention that the mixtures with a low thermal conductivity mentioned in section 4.3 showed a compressive strength in the range 4,5-6.0 MPa while commercial autoclaved aerated concrete masonry blocks have an average compressive strength above 4,5 MPa.

### Cost analysis

Since the sodium perborate has a cost 50% higher than the hydrogen peroxide it is important to assess how can this influence the overall cost performance of the different mixtures. Fig. 5 shows the cost of the foam geopolymer mixtures according to the activator/binder ratio and sodium silicate/sodium hydroxide mass ratio. The lower the activator/binder ratio, the lower the sodium silicate/sodium hydroxide ratio, the lower the foaming agent content the lower the cost. This is because the cost percentage of foaming agents is just around 10% the total cost. Alkaline activators being responsible for 80% of the cost.

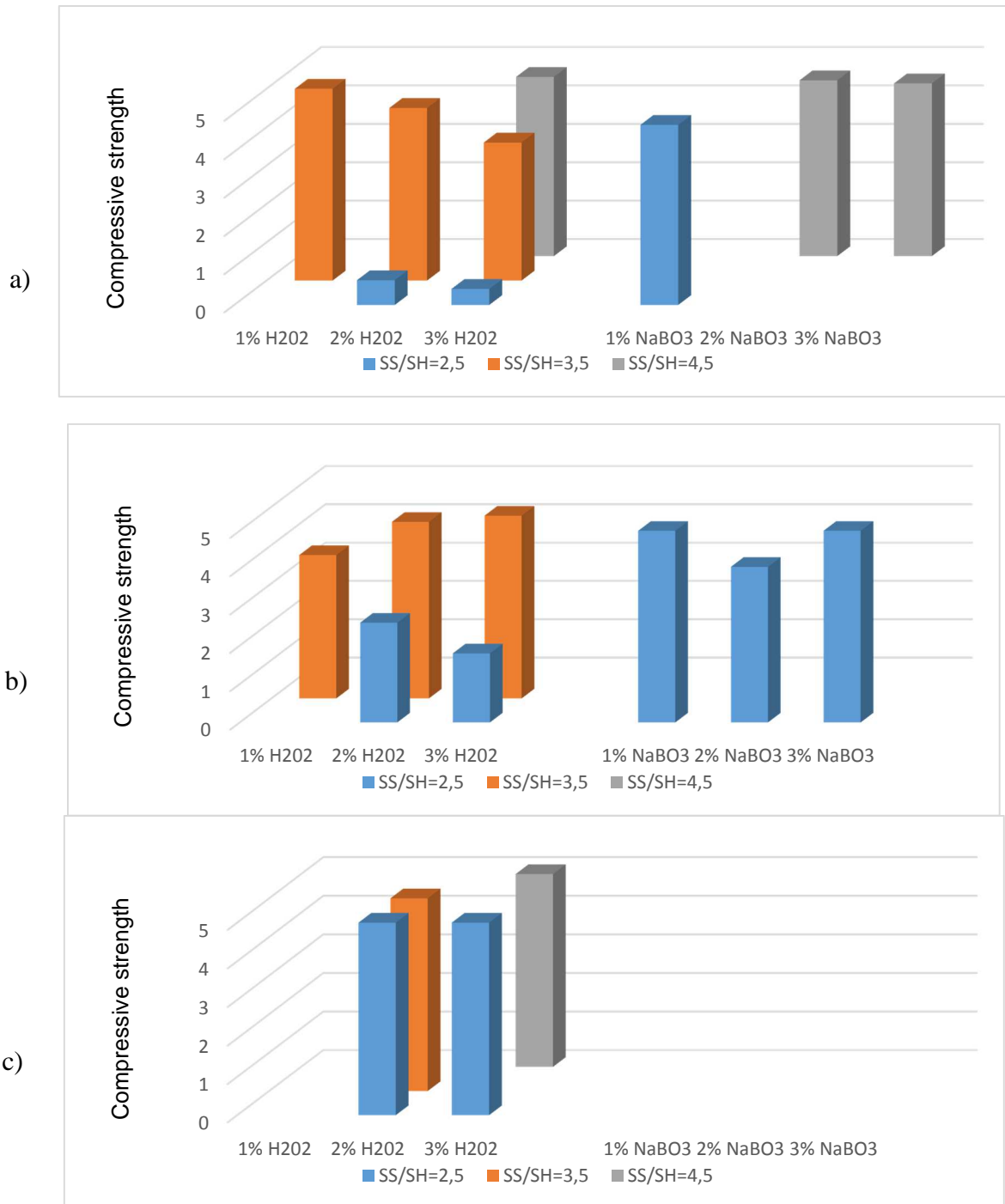


Fig. 4 – Compressive strength according to activator/binder ratio and sodium silicate/sodium hydroxide mass ratio: a) Activator/binder ratio=1; b) Activator/binder ratio=0.8; Activator/binder ratio=0.6



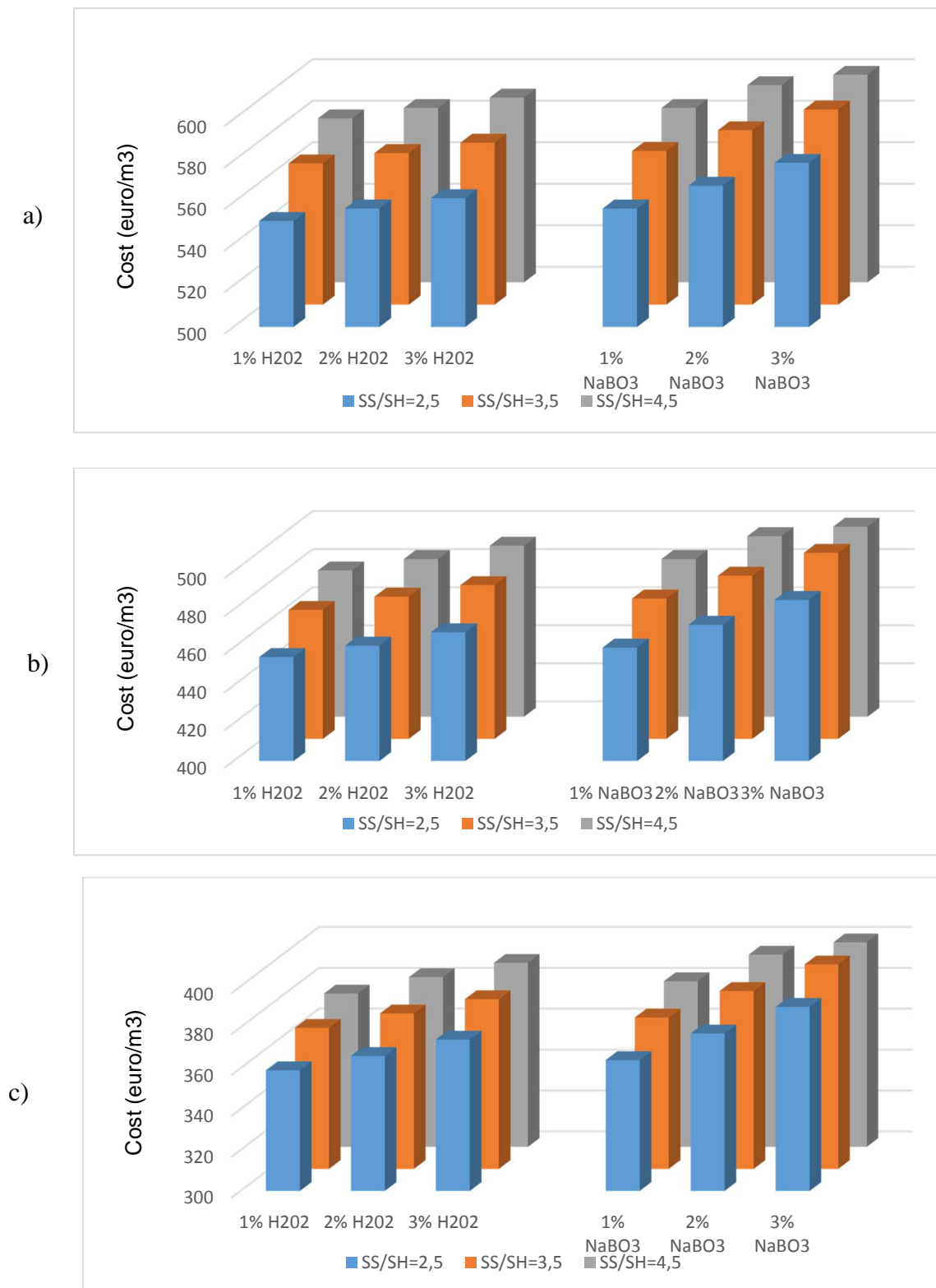


Fig.5 – Cost according to activator/binder ratio and sodium silicate/sodium hydroxide mass ratio:  
 a) Activator/binder ratio=1; b) Activator/binder ratio=0.8; Activator/binder ratio=0.6

Fig 6 shows the cost to thermal resistance ratio. The best mixture use sodium perborate with a activator/binder ratio of 1.0 and sodium silicate/sodium hydroxide mass ratio of 4.5. Hydrogen peroxide based mixtures (3% and 2% content) with and activator/binder ratio of 0.8 and a sodium silicate/sodium hydroxide mass ratio of 2.5 and 3.5 also present a low cost to thermal resistance ratio.

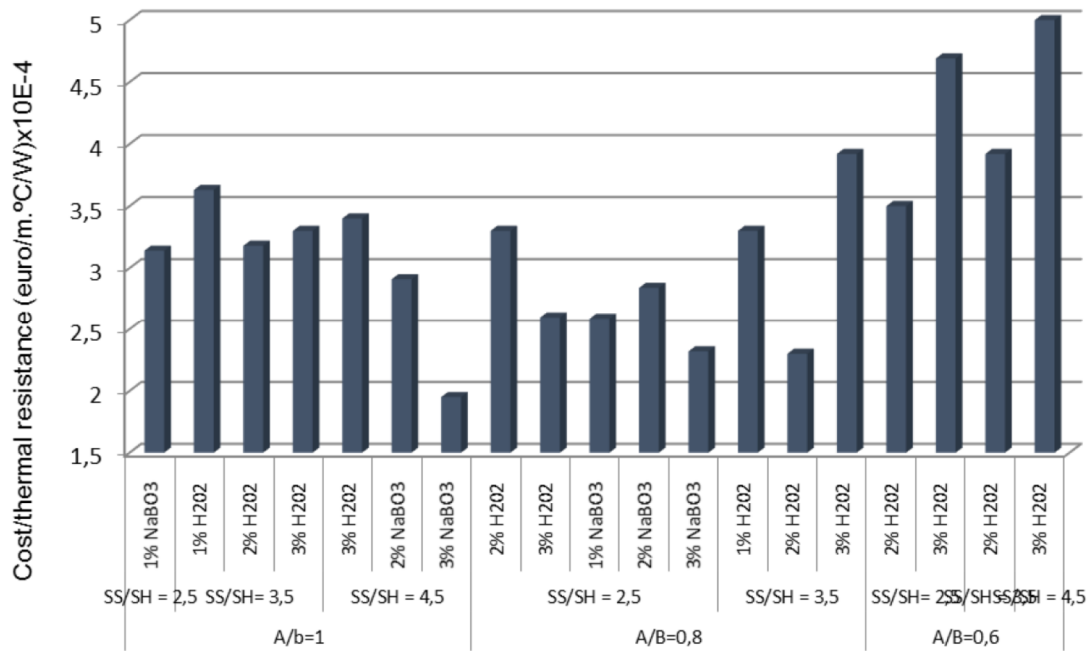


Fig.9 – Cost to thermal resistance ratio

### Conclusions

The increasing demand for worldwide energy, is a major cause for the unsustainable development of our Planet. The use of thermal insulation materials constitutes the most effective way of reducing heat losses in buildings thus reducing heat energy needs. However, current insulation materials are associated with negative impacts in terms of toxicity. Not only during the production phase but also releasing toxic fumes when subjected to fire. This paper discloses results of a study that has investigated the joint effect of several mix parameters on the properties of foam geopolymers fly ash-based. The results show that the sodium perborate over performs hydrogen peroxide leading to a lower overall thermal conductivity of foam geopolymers. The use of an activator/binder ratio of 0.8 a sodium silicate/sodium hydroxide of 2.5 led to the lowest thermal conductivity. Mixtures with a low thermal conductivity of around 0.1 W/(m.°K) and a compressive strength of around 6 MPa were achieved. The cost analysis show that the foaming agents are responsible for a small percentage of foam geopolymers total cost (less than 10%) being that the alkaline activators are responsible for more than 80%.

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