

## The Effects of Foaming Agents and Modifiers on a Foamed-geopolymer

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### ABSTRACT

The geopolymers are not only stronger and less damaging to the earth, but they can also be made with byproducts of other industries such as slag and fly ash. In this study, zinc and aluminum powders were used as foaming agents and organosilane was innovatively used as a modifier to synthesize a foamed geopolymer. This environmentally friendly foamed geopolymer is an ideal building material for fire resistance, sound absorption and thermal insulation for enhanced compressive strength and low thermal conductivity. It was achieved by adding the modifier and increasing the porosity in the foamed geopolymer, respectively. The total pore volume is greatly increased by releasing the hydrogen gas in the foamed geopolymer, which was made from the chemical reaction of zinc and aluminum powders in a base solution. The role of modifier is to slow down the foaming reaction rate and to form the homogeneously-distributed small pores in the foamed geopolymer with improved compressive strength. The modifier-enhanced foamed geopolymer with 0.8% of zinc powder has great building material characteristic of low thermal conductivity (0.113 W/m.K) and high compressive strength (> 3.7 MPa).

### 1. INTRODUCTION

The geopolymer material was made from the geosynthesis of alkali-activated aluminosilicate materials, which produced a three-dimensional polymeric structures of linked SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra (Davidovits, 1994). Geopolymer binders and geopolymer cements are generally formed by reaction of an aluminosilicate powder with an alkaline silicate solution at roughly ambient conditions. Metakaolin is a commonly used starting material for laboratory synthesis of geopolymers, and is generated by thermal activation of kaolinite clay (Wikipedia, 2011). A solution of sodium hydroxide or potassium hydroxide must be prepared separately, then added to the liquid commercial sodium silicate; this solution may then be added to the metakaolin or powdered coal fly ash. Geopolymer materials and geopolymer cement blends can be used for many applications, such as fire and acid resistance, various structural materials, heavy metals immobilization, metal and ceramic surfaces bonding, etc. (Geopolymer institution, 2011).

The foamed geopolymer materials have characteristics of lightweight and heat insulation because of many micro-porous structures (Davidovits, 1981). The physical properties of the hardened geopolymer are influenced by the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the geopolymer network. In the past, foamed geopolymers are prepared by compositional water expelled bubbles at a high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (over than 24, even to 300) (Fletcher,

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et al., 2005). Then, increased heating of geopolymers, from 100°C to 300°C, or even 500°C, is required to form bubbles (Oudadesse, et al., 2007) and this process is energy-consumption. Nevertheless, another type of porous lightweight geopolymer has been extensively studied due to its low cost, sinter-free fabricated, acid resistance, good thermal properties and environmentally friendly nature (Liu, 2010). Therefore, foamed geopolymers can be produced by adding a foaming agent (Davidovits, 1981) such as peroxides, perborates, etc. (Liefke, 1999). However, chemical reaction induced foamed geopolymers usually have weak mechanical properties because of a large pore size distribution of about 0.5-3.0 mm (Liefke, 1999). This phenomenon has resulted in restrictions on its applications. The larger pore size (about 0.5-3.0 mm) is created by the release of O<sub>2</sub> gas during H<sub>2</sub>O<sub>2</sub> decomposition. If the released bubble size can be efficiently controlled, the mechanical strength of the foamed geopolymer will be improved.

In this study, active metal powders and an organosilane water repellent agent were used as the foaming agents and a modifier in the preparation of the foamed geopolymers, respectively. The active metal powder reacted with sodium hydroxide to release smaller hydrogen and cause the pore formation within the geopolymer matrix. As a result of the addition of the proper modifier, a fine and homogeneous pore size distribution was produced. The pre-forming soundproof geopolymer building materials could be made, and the improvement of living quality and comfort will be reached by such a light-weighted, compressible, fire-resistant and soundproof green materials. The influences of the foaming methods, the constitution of source powders, base solution ratio, the procedure sequences, category of forming agents and stabilizers on the physical properties of the pre-forming geopolymer building materials should be noted. In this study, the microstructure, thermal conductivity, compressive strength, and bonding conditions of the foamed geopolymers were discussed below.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials and methods

The desired amounts of sodium hydroxide pellets (81.7 g) and sodium silicate solution (263 mL) were mixed together to prepare the liquid portion of 500 mL. The sodium silicate solution (water glass) contained 31.8% SiO<sub>2</sub>, 12.4% Na<sub>2</sub>O and 55.8% H<sub>2</sub>O. 10% of sodium silicate solution was added to a sodium hydroxide solution, and the produced alkali modulus (SiO<sub>2</sub>/Na<sub>2</sub>O ratio) was 1. The equivalent alkaline content was 30% (by Na<sub>2</sub>O) and water-binder ratio was 0.7. The modifier was added after the solution was mixed. An alkoxy silane water-based emulsion (Z6688, water repellent gel, Dow Corning) was used as modifier. Then, metakaolin was added slowly into the base solution to form homogeneous slurry. The metakaolin was prepared by the calcination of kaolin at 700°C for 3h. The liquid/solid ration was adjusted until it was 2:1. After completely mixing the metakaolin and the base solution, the foaming agent (below 325 mesh of aluminum or zinc powders) was added to the slurry. The slurry was poured into a cylinder mold until it was stable. The completely mixed samples were hardening and removed from the mold after 1 week for aging at room temperature. After 28 days' curing to dry at room temperature, the thermal conductivity and compressive strength were measured to investigate the characteristics of foamed geopolymer. The metakaolin powders were analyzed using an atomic absorption spectroscopy (AAS) and composition distribution is listed in [Table 1](#). The main compositions are aluminum oxide (55.87%) and silicon oxide (42.68%). These two compounds are geopolymer

materials and accounted for 98.55%.

**Table 1** composition distribution of an as-prepared metakaolin

Components	Weight ratio (%)
Al <sub>2</sub> O <sub>3</sub>	55.87
SiO <sub>2</sub>	42.68
P <sub>3</sub> O <sub>4</sub>	0.27
K <sub>2</sub> O	0.05
CaO	0.07
TiO <sub>2</sub>	0.66
Fe <sub>2</sub> O <sub>3</sub>	0.28
Loss on ignition	0.12
Total	100.00

### 2.2. Analysis

The surface morphology of the foamed geopolymer was observed with a high-resolution scanning electron microscope (HR-SEM, Hitachi S4100, Japan). The sample was grinded and then carbon-coated on the carrier for SEM use. The structure and bonding of foamed geopolymer samples was investigated by Fourier Transform infrared (FTIR, JASCO FT-IR-460 plus, Japan) spectroscopy within the frequency range of 4000-400cm<sup>-1</sup>. The samples were ground to about 5-10 μm powder and then mixed into a paste with drops of paraffin oil for FTIR use. The FTIR spectra were obtained with a sensitivity of 4cm<sup>-1</sup> with 8 scans per spectrum taken. Furthermore, the most commonly studied nuclei is <sup>13</sup>C, although nuclei from isotopes of the other element (e.g., <sup>29</sup>Si, has been studied by high-field NMR spectroscopy as well in this study). The spectral unit is ppm. The bulk densities of the foamed geopolymers were measured using the Archimedes method in deionized water. The compressive strength was measured using an auto-compressive strength tester (ELE ADR-Auto Range 9901X0215, Japan) with an applied load speed of 5\*10<sup>5</sup>~7\*10<sup>5</sup> N/mm<sup>2</sup>/min. Specimens were cylindrical with 50 mm in diameter and 100 mm tall. Thermal conductivity was measured with a thermal conductivity analyzer (Applied Precision ISOMET 2104).

## 3. RESULTS AND DISCUSSION

### 3.1. Structure and composition observations

**Fig. 1** showed the SEM microstructure of the non-foamed and foamed geopolymer. The non-foamed geopolymer morphology contains three different structures: plate structure, fine-grained, and white precipitate. According to the reference (Kriven, et al., 2003), plate precipitate is caused by incompletely reacted geopolymer, and the fine-grained structure is attributed to the completely reacted geopolymer. However, the white precipitate was produced by the Na<sup>+</sup> that was not to bond with Si-O and Al-O (non-bridge) and the remaining Na<sup>+</sup> reacted with carbon dioxide in the atmosphere to form the sodium carbonate (Rees, et al., 2008). In addition, the pore size distribution range was about 0.1~0.3 mm from the SEM microstructure of modifier-added foamed geopolymer. The Si/Al ratio (31.03/15.84) was about 2 for the non-foamed geopolymer from SEM/EDS test.

**Fig. 2** showed the macrostructure of the foamed geopolymer and the modifier-added foamed geopolymer. The foamed geopolymer induced with metal powders contains various pore sizes. The pore size increases from bottom to the top, or from the inner to outer regions of the samples. However, fine uniform pores were observed after adding

the modifier to the foamed geopolymer (left side of Fig. 2). During the preparation of the foamed slurry, H<sub>2</sub> bubbles were released more slowly in the modifier-added series than in the non-modifier-added series. The slow gas release rate was responsible for the smaller and uniform pore distribution in the foamed geopolymers.

Fig. 2 also showed the rough pore size distribution ranges about from 0.5~5 mm in the metal powders-foamed geopolymer. However, smaller pores (i.e., 0.1~0.3 mm) accompanied by a low ratio of large-sized pores can be seen in the modifier-added geopolymer. The cracks in the morphologies propagate from the larger pores to the neighboring pores in the metal powders-foamed geopolymer, but cracks do not propagate through the small pores in the modifier-added geopolymer. Almost no large-sized pores may improve the compressive strength of the modifier-added geopolymer. It can be expected that Al- or Zn-foamed geopolymer have higher Al and Zn ratios than a non-foamed geopolymer due to the addition of Al or Zn powders from SEM/EDS results of the metal powders-foamed geopolymers and the modifier-added geopolymer. On the other hand, the modifier-added geopolymer has a higher Si/Al ratio as result of the increase in the Si content from the organosilane modifier.

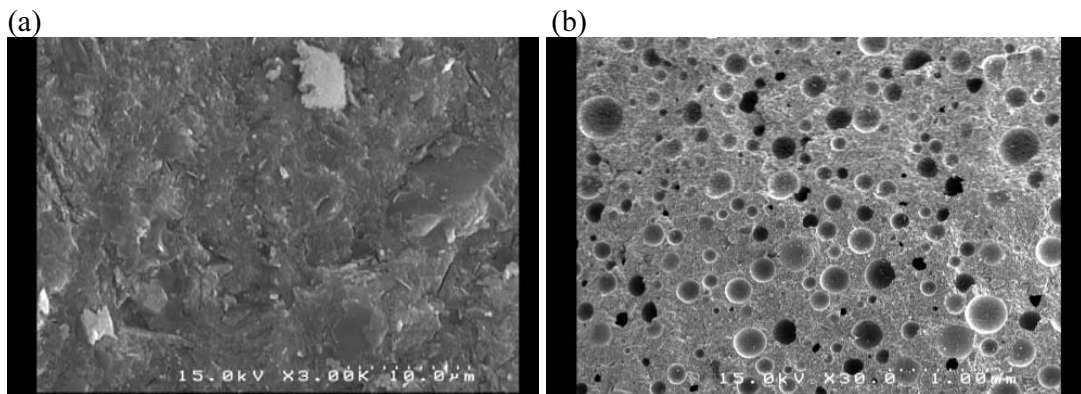


Fig. 1 the SEM microstructure of (a) non-foamed geopolymer and (b) modifier-added foamed geopolymer



Fig. 2 the macrostructure of the metal powders foamed geopolymer (the right side) and the modifier-added foamed geopolymer (the left side)

### 3.2. Density property

Fig. 3 showed the density values of Al-foamed, Al+modifier foamed, Zn-foamed, Zn+modifier foamed geopolymers. The density data shown in Fig. 3 is average data, and the repeated analysis of the differences are within 20%. The density of non-foamed geopolymer was about 1000~1180 kg/m<sup>3</sup>. An increase in the amount of the metal (Al or Zn) powders resulted in a foamed geopolymer with low density. The metal activity of aluminum is greater than the activity of zinc metal. Therefore, the aluminum powder had high reactivity with sodium hydroxide (Geopolymer institute website, 2011). It produced more hydrogen as a result, which reduced the density more quickly than in the case using zinc powders, as seen in Fig. 3. All of the modifier-added geopolymers had lower densities than the metal powder-added geopolymers. It was also found that densities dropped more quickly in the case of the zinc+modifier foamed geopolymer. The organosilane modifier in the base solution caused a hydrolysis and condensation reaction, which released water or alcohol, both of which induced extra pores in the foamed geopolymer (Davidovits, 2008).

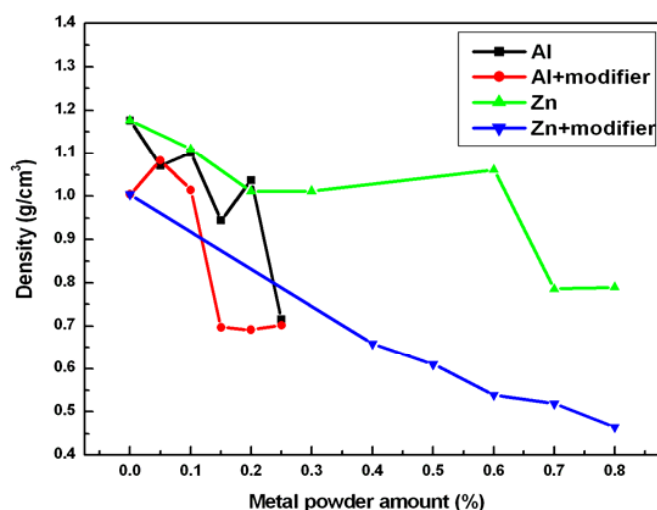


Fig. 3 the density values of various foamed geopolymers

### 3.3. FTIR analysis

Fig. 4 showed the FTIR results of non-foamed and foamed geopolymers. According to the study (Davidovits, 2008), the peak at 1065 cm<sup>-1</sup> belongs to the asymmetric stretching vibration of the Si-O-Si and Si-O-Al, and high amounts of aluminum inclusion occur as the peak shifts to a lower wavenumber. All the Al-foamed geopolymers concur with this finding. This is also consistent with the previously referenced SEM/EDS results: the Al% increase in the aluminum-foamed geopolymer. The broadened peak around 3440-3480 cm<sup>-1</sup> is attributed to molecular water absorbed into the surface of the geopolymer (absorbed O-H stretching). No broadened peak appeared in the modifier-added geopolymer. Because a hydrophobic water repellent agent was added, the surface of the geopolymer did not absorb water from the atmosphere. It is noted that a small peak appears at 1420-1480 cm<sup>-1</sup>. It was defined as the vibrational stretching frequency of the C-O in the carbonate, and caused by the unreacted alkali cations and the dissolved CO<sub>2</sub> (Davidovits, 2008). The addition of the modifier may caused a reaction with the alkaline solution that affected the bonding of



Al-O or Si-O with sodium.

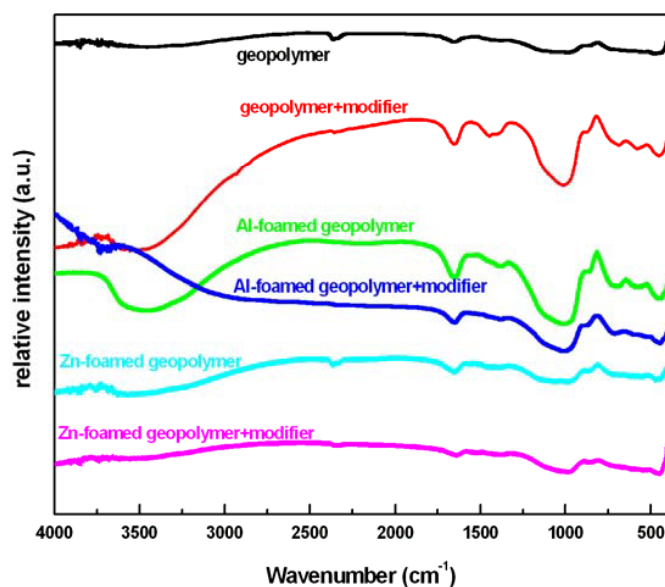


Fig. 4 the FTIR results of non-foamed and foamed geopolymers

### 3.4. Thermal conductivity measurement

Fig. 5 showed the thermal conductivity values of various foamed geopolymers. The thermal conductivity data shown in Fig. 5 is average data, and the repeated analysis of the differences are within 20%. It was found that the addition of more metal powders to the foamed geopolymer resulted in lower thermal conductivity, which was caused by higher porosity. Furthermore, the modifier-added geopolymer had lower thermal conductivity than the metal powder-added geopolymer. According to the SEM observation, the modifier-added geopolymer had more micro-pores between the large pores, and this was one of the main reasons for the drop in thermal conductivity. The lowest thermal conductivity (0.113 W/m.K) occurred in the modifier-added geopolymer with a 0.8 % zinc addition.

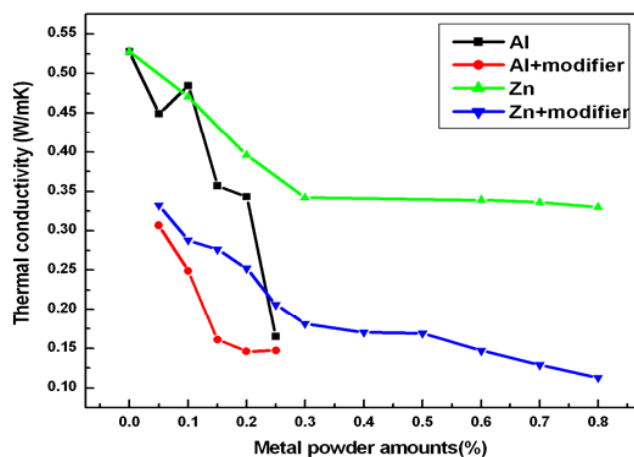


Fig. 5 the thermal conductivity comparisons of the various foamed geopolymers by

different metal powders

### 3.5. Compressive strength measurement

Fig. 6 showed the compressive strength values of various foamed geopolymers. The compressive strength data shown in Fig. 6 is average data, and the repeated analysis of the differences are within 20%. The compressive strength was improved in the zinc-modifier foamed geopolymer, but was decreased in the aluminum-modifier foamed geopolymer. The larger proportion of large-size pores in the microstructure caused the weak compressive strength of the aluminum-modifier foamed geopolymer. According to the reference (Liu, et al., 2010), the maximum compressive strength is 7MPa about 83% porosity value. The results of this study are similar to the reference (Liu, et al., 2010).

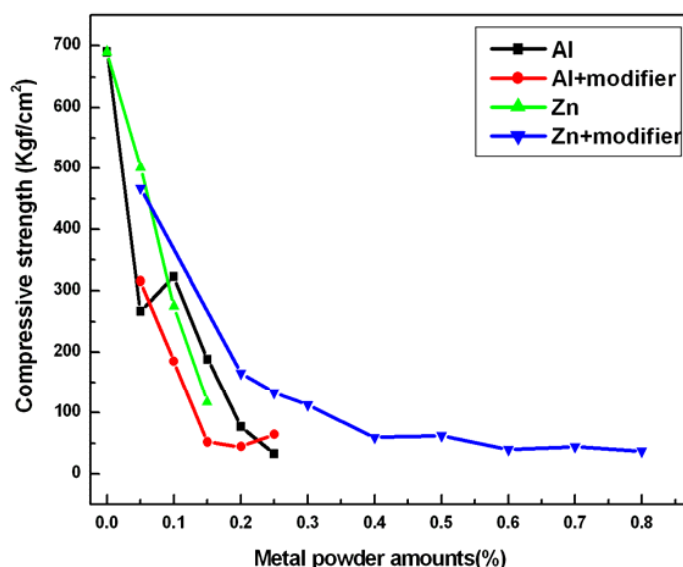


Fig. 6 the compressive strength comparison of the various foamed geopolymers by different metal powders

### 3.6. Liquid-state NMR measurement

The modifier used in this study was a monomeric medium-chain alkyl functional silane, n-octyltriethoxysilane, (Dow Corning Z6688 water repellent gel). The hydrolysis reaction occurred as it reacted with water or moisture and produced ethanol. Hydroxyl groups formed as Z6688 under acidic or base condition, and bonds to substrate to formed a hydrophobic surface.

In order to identify the possible reaction process of adding the modifier during geopolymerization,  $^{29}\text{Si}$  and  $^{13}\text{C}$  liquid-state NMR were used to analyze the modifier (Z6688) and a mixture of Z6688, water glass, and sodium hydroxide (Z6688 in a base solution), as shown in Fig. 7 and Fig. 8.

Fig. 7 showed the  $^{29}\text{Si}$ -NMR results of organosilane and it mixed in a base solution. The organosilane transferred to various dimeric or oligomeric structures during the polycondensation reaction in the presence of chemical bondings  $\text{T}^0\sim\text{T}^3$ . After adding the organosilane to the base solution, the  $\text{Q}^0\sim\text{Q}^4$  peaks of the water glass were the predominant bondings in the spectra. The  $\text{T}^0\sim\text{T}^3$  peaks of the organosilane were suppressed as result of the high proportion of water glass in the base solution.

Fig. 8 showed the  $^{13}\text{C}$ -NMR results of organosilane and that in the base solution. All

the carbon bonds appeared in the Z6688 solution and only the O-CH<sub>2</sub>-CH<sub>3</sub> bondings appeared in the Z6688 in base solution. It is presumed that the long-chain carbon bonding was broken after Z6688 was mixed with the base solution.

According to the liquid-state NMR results, the possible reaction mechanisms of the modifier induced foamed geopolymer are shown in Fig. 9. The hydrolysis reaction occurred as Z6688 was added into the base solution and the hydroxyl based organosilane was formed. Because the hydroxyl groups existed on the surface of the activated metakaolin, the hydrogen bonding formed between the hydrolyzed organosilane and metakaolin. The hydrophobic end of the organosilane was trapped in the hydrogen gas and distributed the bubbles uniformly throughout the foamed geopolymer slurry. After the setting treatment, the modifier induced foamed geopolymer thus contained homogeneously distributed porosity.

Table 2 shows a comparison of the physical properties of the commercialized foamed geopolymer (Liefke, 1999) and the one produced in this study. The compressive strength and thermal conductivity of the foamed geopolymer in this study is comparable in ability with the available commercial product. It is demonstrated by the high compressive strength and suitable thermal conductivity. The uniform and small pore-size distributions were produced in the foamed geopolymer because of the slow release of a small amount of hydrogen gas by the added metal powders and modifier. Therefore, the resulting compressive strength is greater than that of the commercial foamed geopolymer (Liefke, 1999). In the future, by controlling suitable metal powders and modifier amounts, superior thermal conductivity and enhanced mechanical strength in foamed geopolymers will be applied as characteristics of useful materials in various applications.

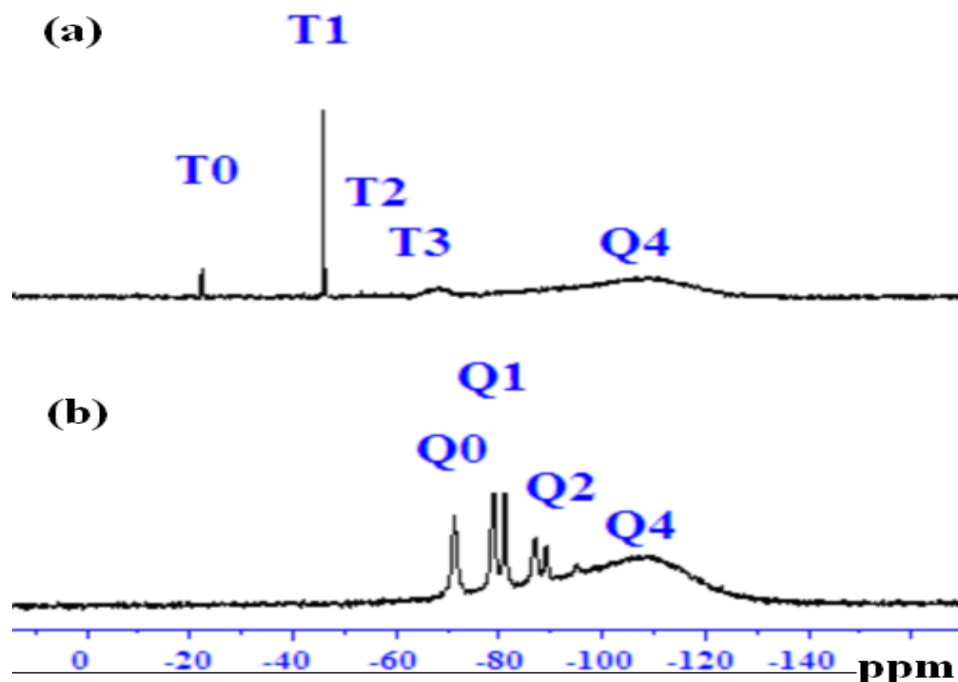


Fig. 7 <sup>29</sup>Si-NMR results of (a) organosilane and (b) organosilane in the base solution



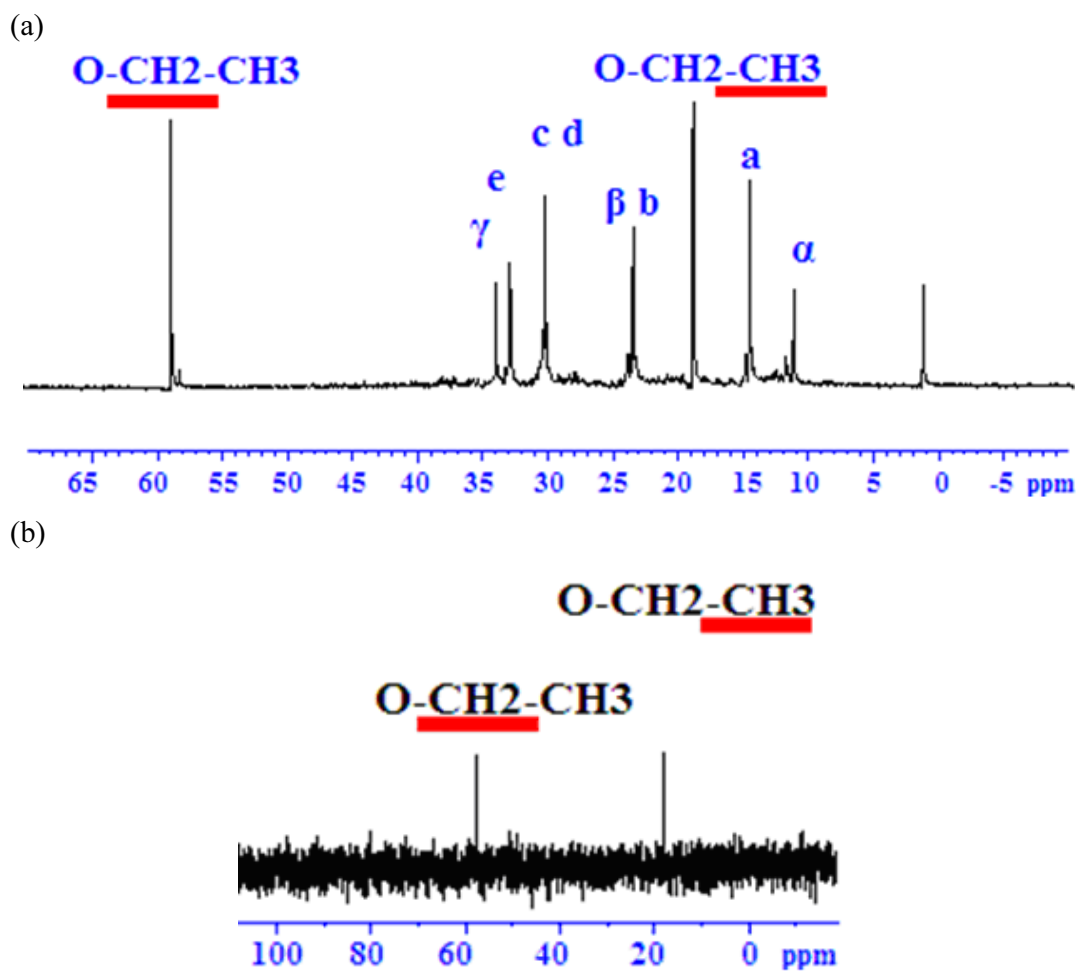


Fig. 8  $^{13}\text{C}$ -NMR results of (a) organosilane and (b) organosilane in the base solution

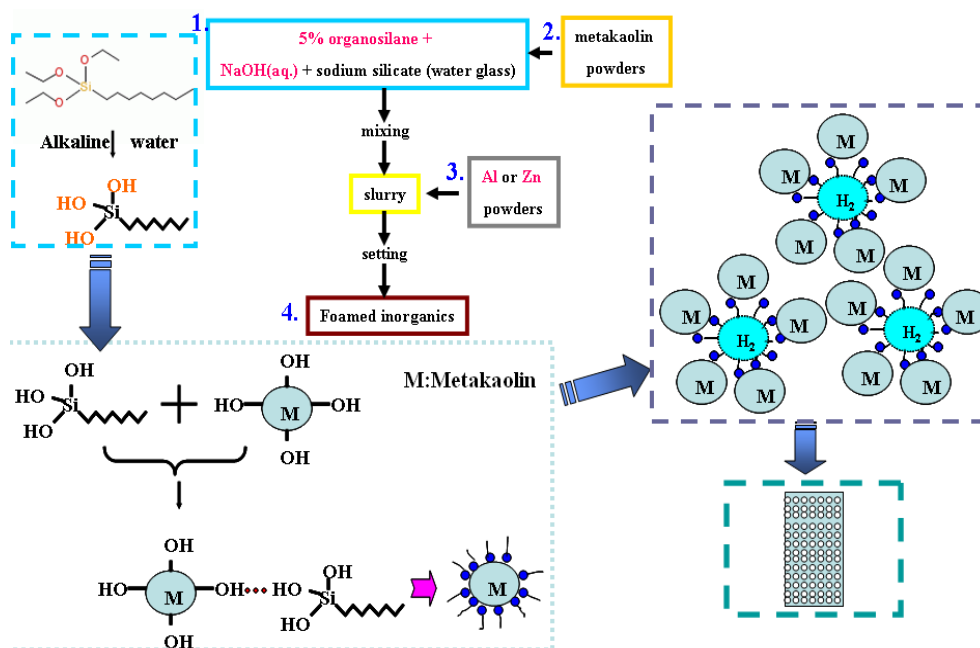


Fig. 9 the possible reaction mechanism of modifier induced foamed geopolymer

**Table 2** A comparison of the physical properties for TROLIT inorganic foams and the one in this study

Product	TROLIT	This study
Bulk density (g/cm <sup>3</sup> )	0.1-0.8	0.4-1.0
Compressive strength (Kgf/cm <sup>2</sup> )	5-20	37-467
Thermal conductivity (W/mK)	0.037*	0.113*

\* Depending on density

## CONCLUSIONS

Foamed geopolymers were successfully prepared by adding metal powder and an organosilane modifier. The modifier induced micro-pores in the geopolymer matrix, and enhanced thermal resistance and the proper compressive strength. Through the addition of a suitable metal powder and an appropriate modifier, the resulting foamed geopolymer can be used as great building material for fire resistance, sound absorption, and thermal insulation.

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