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Chemical retreating for gel-typed aerogel and insulation performance of cement containing aerogel

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HIGHLIGHTS

- ▶ Possibility of new type of cement composite using aerogel was studied.
- ▶ Gel-typed aerogel was prepared by methanol to mix with cement stably.
- ▶ No chemical changes of aerogel cement were confirmed by FT-IR and SEM.
- ▶ Thermal conductivity of aerogel cement decreases by 75% comparing to ordinary one.

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ABSTRACT

This research identified the possibility of application as an insulation building material by mixing aerogels with the cement paste as well as their thermal performance. The aerogel is a very stable material against water because of their skeleton's characteristics, so that re-treatment of aerogel had to be preceded before mixing with cement pastes. Chemical and physical stability caused by the re-treatment of aerogel in the cured cement were confirmed by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM). Moreover, thermal conductivity of aerogel cement was 0.135 W/m K which is 75% of aerogel-free cement's thermal conductivity, 0.533 W/m K.

1. Introduction

The demand for energy is increasing as a result of increasing population, expansion and development plans, and maintaining a good indoor thermal comfort conditions. Besides, the increasing cost of energy and adverse impact on the environment by energy production plants, all contribute to the need to find means to substantially reduce energy consumption. Buildings, through cooling and heating requirements, are major contributors to energy consumption worldwide. It is estimated that about two-thirds of the energy is used in buildings [1,2]. In order to prevent these current situations, building envelope is very important building components to provide thermal comfort for the residents as well as reduce energy consumption to maintain indoor conditions.

Aerogels, nanoporous lightweight materials, were discovered in the early 1930s [3]. The processes of principle and preparation were extensively described by Brinker and Scherer [4]. The main precursors for silica aerogels are silicon alkoxides. Tetramethoxysilane $Si(OCH_3)_4$ or TMOS [5], tetraethoxysilane $Si(OC_2H_5)_4$ or TEOS and polyeth xydisiloxane $SiO_n(OC_2H_5)_{4-2n}$ or PEDS-P_x [6] are most often used, where PEDS-P_x can be obtain by reacting TEOS with a substoichiometric quantity of water in an acidic alcoholic medium according to

$$Si(OCH_3)_4 + nH_2O \leftrightarrow SiO_n(OC_2H_5)_{4-2n} + 2nC_2H_5OH \quad (1)$$

for n lower than 2. From the point of view for application as thermal insulation, the thermal conductivities of PEDS and TMOS aerogel monoliths will be found lower compared to TEOS aerogel monoliths, whereas high-quality transparent aerogels have been developed based on TEOS. Additional solvents such as methanol are needed with much water will yield low-porosity gels [7,8].

Now, aerogel is a promising material with exceptional physical properties to be used in technologically advanced products. During the years, a wide range of potential applications were described in the field of insulation, chemistry, kinetic energy absorber, electronics, pharmacy, agriculture and filler [9]. Due to its extraordinary small pore sizes and high porosity, the aerogel achieves its

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remarkable physical, thermal, optical, and acoustical properties. The high porosity makes aerogels the light solid material, and aerogels have load bearing with high compression strength up to 3 MPa [10]. Among its characteristics, the low thermal conductivity and stability were the most distinguished merits. However, the traditionally practiced supercritical production process and normally used expensive raw materials prevented a production in an industrial scale due to cost [11,12].

These days, most of traditional insulation products which are made of the polystyrene and composite materials laminated with the organic and inorganic substances have been used in the building and manufacture fields because of affordable prices to reduce amount of construction costs. However, the traditional insulation materials were and are being used in thicker or multiple layers which result in more complex building details, an adverse net-to-gross floor area and possible heavier load bearing constructions [13]. Besides, where the insulation materials are used by themselves in buildings, there is a negative behavior not to show their insulation performances in case of absorbing the leakage water or vapors through the air flow for long time, being damaged by external impacts, or releasing toxic gases during a fire. Therefore, the traditional insulation materials should be sought to transfer to a new approach to compensate those defects for the sustainable building in term of the effective construction, healthy space and energy savings.

Even though the high prices of aerogels interrupt a plenty of application in building materials, the continuous cut in production costs due to improvements of manufacturing process with keeping aerogel's merits. Therefore, above problems can be solved by using a cement type insulation to contain aerogels as the non-structural component for energy savings and supplementation the shortcomings of common insulation products. For the characterized purpose, the properties of aerogel cement (AC) with different amount of aerogels were studied.

2. Materials and experimental methods

2.1. Materials

In this work, ordinary Portland cement, according to KS L 5102 [14], was used and supplied by Asia Cement Co., Seoul, South Korea.

The powder-type silica aerogel manufactured by EM-POWER CO., LTD. in Korea have been used. Table 1 [15] shows the physical properties of aerogel. The reasons aerogels have the low thermal conductivity λ_{tot} (W/m K) are resulting from low solid skeleton conductivity, a low gaseous conductivity λ_g and a low radiative infrared transmission T_{IR} [16,17]. Surface area and pore size distribution of aerogel were measured by Brunauer–Emmet–Teller (BET). The pore size distribution of aerogels is shown in Fig. 1. It can be seen that aerogels have a wide pore size distribution, which is mainly composed of micropores.

2.2. Specimen preparation

The preparation of gel-typed aerogel was processed in which solid nanoparticles dispersed in a liquid agglomerate together to form a continuous three-dimensional network extending throughout the liquid. Aerogels have the super hydrophobic solid framework so that it is impossible for these to mix with the cement pastes, cement and distilled water. In addition, the mechanical strengths of AC can be dramatically decrease by the physical properties of aerogel; low density, large porosity and pore size which would have possibility to generate large and many cracks in AC. Therefore, gel-typed aerogel prepared by methanol were needed not only to mix with cement pastes stably but also to reduce cracks between the hydration particles to have the effect on the compression and flexural strength connections of AC. The mass ratio of aerogel and methanol for gel-typed aerogel was 1:0.7 which was determined by their molar ratio. The prepared gel-typed aerogel was directly mixed with cement paste, and they were cured together for 28 curing days.

Table 1
Physical properties of aerogel [16].

Particle size	1–10 μm
Surface area	700–800 m^2/g
Tap density	0.05 g/cm^3
Porosity	95%
Pore volume	1.97 cm^3/g
Pore size	109.50 nm
Thermal conductivity	0.02 W/(m K)

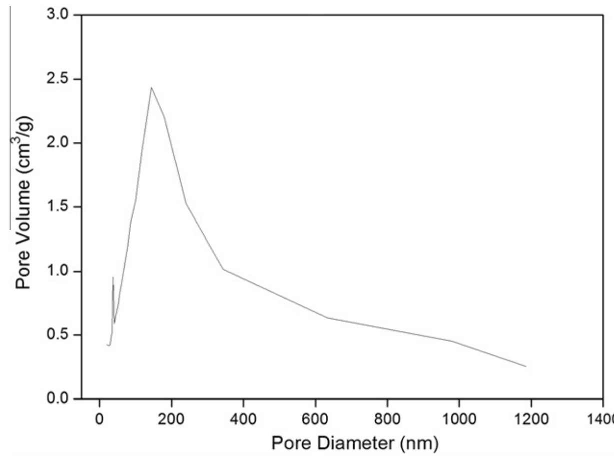

Fig. 1. Pore size distribution of aerogel.

Different values of aerogel were prepared as percentages of cement mass content, ranging from 0.5 to 2.0 wt.%. Water/Portland cement ratio was always 1:2. Also, 20% of pozzolan which is mainly composed by SiO_2 and Al_2O_3 was substituted for cement to prevent detrimental expansion of hardening cement samples. Mortars were prepared at laboratory ambient conditions according to ISO 679, 20 °C ± 2 °C and 80% RH ± 5% RH. As soon as casting and surface finishing are completed, molds were covered with polyethylene films to keep evaporation of samples water and then stored on the condition, 20 °C ± 1 °C and 90% RH, for 24 h. After that, the samples were stored in water container at 20 °C ± 1 °C for 28 curing days [18].

2.3. Experimental method

In this study, Thermogravimetry analysis (TGA) was carried out to confirm the thermal stability of aerogel at high temperature. TGA was conducted to mass changes of a sample of material, as a combination of temperature with time, and additionally of pressure and gas composition. The temperature was increased from 30 °C to 1150 °C with intervals of 10 °C/min.

Chemical and physical stability caused by the re-treatment of aerogel in the cured cement were confirmed by Fourier transform infrared spectroscopy (FT-IR) in accordance with the modification process and scanning electron microscope (SEM). The FT-IR spectrum data to determine the chemical stability were obtained with FT-IR 6100 equipment produced by JASCO. The micro photographs of the physical stability of aerogels were taken by SEM, JEOL JSM-6360A, with 20 kV accelerating voltage.

TCi (Fig. 2) developed by C-Therm is a device for conveniently measuring thermal conductivity of a small sample by using the MTPS method. Contrary to other devices, TCi can measure the thermal conductivity of materials in the states of solid, liquid, powder, and mixed. In addition, it can measure thermal conductivity using only one side [19,20]. All kinds of samples of 100 × 100 × 20 mm size were conducted to five times tests of thermal conductivity.

All samples, of 40 × 40 × 160 mm size, were tested for mechanical properties taken directly from the storage container. Three specimens were tested by Universal Test Machine (UTM) as bending with single loading point. The maximum breaking load speed was 50 N/s. Six specimens, the specimens sections obtained from the flexural test, were tested under compression. The crushing load speed was 240 N/s. The method used to determine the flexural and compression strengths of mortar was carried out according to ISO 679.

Absorption test were performed by weighting the specimens in different conditions; dry, saturated in air. The percentage taken up by the absorption in the specimen volume can be found by the following formula; $(\%) = (W_{sat} - W_{dry})/W_{dry}$ with W_{sat} = weight of the specimens saturated in water (with a vacuum pump); W_{dry} = weight of the specimens dried by heating to 120 °C and later cooled into a chemical desiccator.

The flow table tests indicate the consistence of fresh mortar which has an influence on the desired mechanical strength, structural problems caused by cracks and constructability. This test was conducted according to KS L 5111 [21].

3. Results and discussion

3.1. Heat and chemical stability of aerogel cement

The heat stability of aerogel was checked by TGA in accordance with the reaction temperature and gravimetric losses of aerogels.

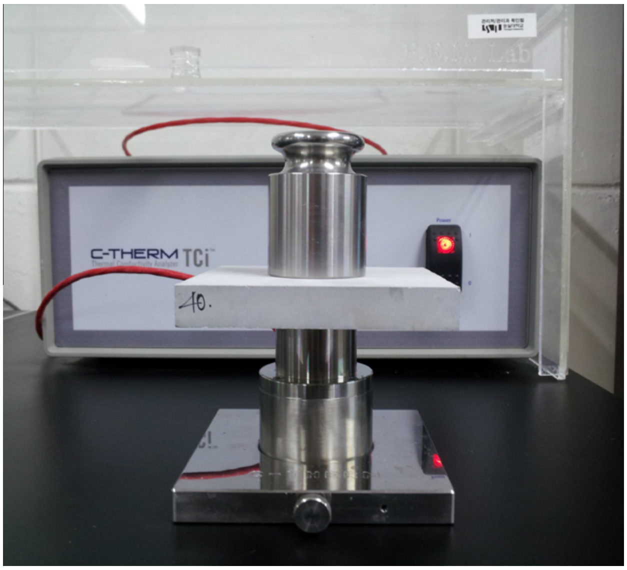

Fig. 2. Thermal conductivity analyzer (TCi).

Temperature from 30 °C to 1150 °C versus gravimetric loss are presented in Fig. 3, and it shows that there was no any changes in mass and no decomposition of aerogel by the temperature reached 1150 °C. This result indicated that aerogel is very stable material at any temperature so that it is possible to apply aerogel to a building fire-resistance cement composite insulation material without emitting noxious gases and its deformation in case of fire.

FT-IR was used to confirm the variation of changes in aerogel's chemical structure on the gel-typed preparation to mix with cement pastes. By observing the three kinds of FT-IR spectrums; aerogel, gel-typed aerogel, and AC, the chemical changes of molecule structure of aerogel on each phase could be found. The FT-IR spectrums are presented Fig. 4. This shows bands assigned to various vibrations in the network. Particularly, there are common peaks at the several specific wavenumbers among the three samples, which demonstrates that there is the same material in each sample. The intense silicon–oxygen covalent bonds vibrations appear mainly in the 1200–1000 cm^{-1} range revealing the existence of a dense silica network, where oxygen atoms play the role of bridges between each two silicon sites. The very intense and broad band appearing at 1095–1089 cm^{-1} and the shoulder at around 1200 cm^{-1} are assigned, which is respectively to the transversal optical (TO) and longitudinal optical (LO) modes of the Si–O–Si asymmetric stretching vibrations [22]. On the other hand, the symmetric stretching vibrations of Si–O–Si appear at around 800 cm^{-1} and its bending mode appears at 469–467 cm^{-1}. The low energy band at around 560 cm^{-1} is assigned to Si–O stretching of the SiO_2 network defects [23,24]. Therefore, the re-treatment step using methanol had a chemical reaction very well during the curing so that the gel-typed aerogel condensed and participated in the formation cement composite. The existing of these bands is the evidence that there is not any chemical molecule change of aerogel on each process; aerogel, gel-typed aerogel and settled aerogel in cement. Because aerogel is very stable materials due to its special properties, so that it is proper process to prepare the gel-typed aerogel by using methanol on putting the aerogel in wide application with other materials stably.

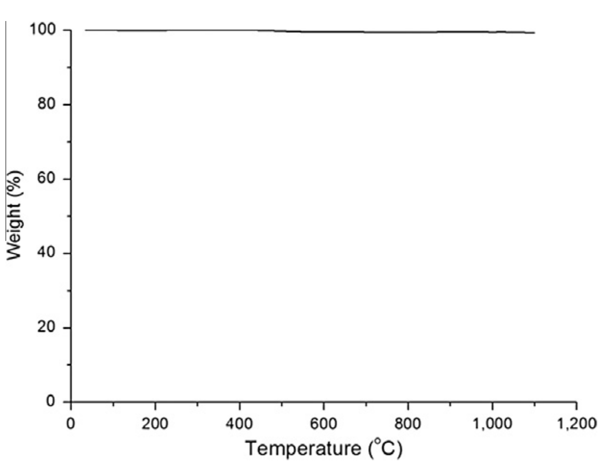

Fig. 3. TGA of silica aerogel (10 °C/min).

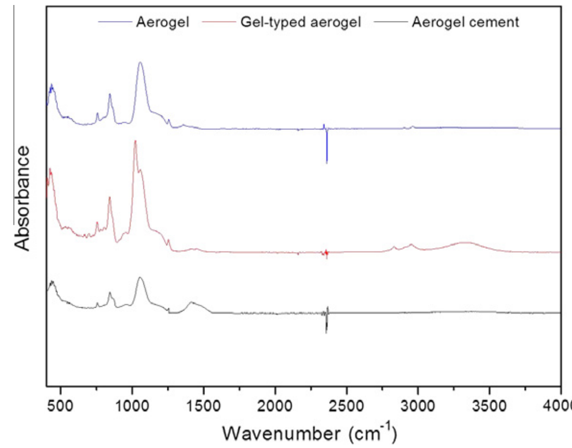

Fig. 4. FT-IR spectroscopy of each type of aerogel.

Fig. 5 shows SEM photographs of cured ordinary cement, aerogel and AC. As shown Fig. 5c, it can be observed that aerogels were stably settled in the cured cement without chemical and physical deformation. As like state above, it is possible to determine that micro physical states of powder-type aerogels in AC were revered from gel-typed aerogels on the preparation process into the cement paste on the grounds.

3.2. Thermal conductivity

Thermal conductivity results of AC and AC with pozzolan are presented in Fig. 6. It is clear that the thermal conductivities of both kinds of samples are 25% of thermal conductivity comparing to the ordinary cement. With increasing aerogel contents, the thermal conductivity of AC is linearly decreased comparing with ordinary cement. As shown Fig. 6, the thermal conductivities of AC show lower value than AC with pozzolan samples generally. Thermal conductivity and the decreasing rate of different types of AC are shown in Table 2. The improved cement composite with high insulation performance by the aerogel has a good probability of decreasing building energy consumption by heating and cooling and enhancing the indoor comfort from molds and condensation on the interior building walls.

3.3. Mechanical properties

As shown in Fig. 7, the relationship between compression strength (R_c, y_1 axis) and absorption (%, y_2 axis) versus aerogel content (wt.%) of AC and AC with pozzolan are presented. With adding

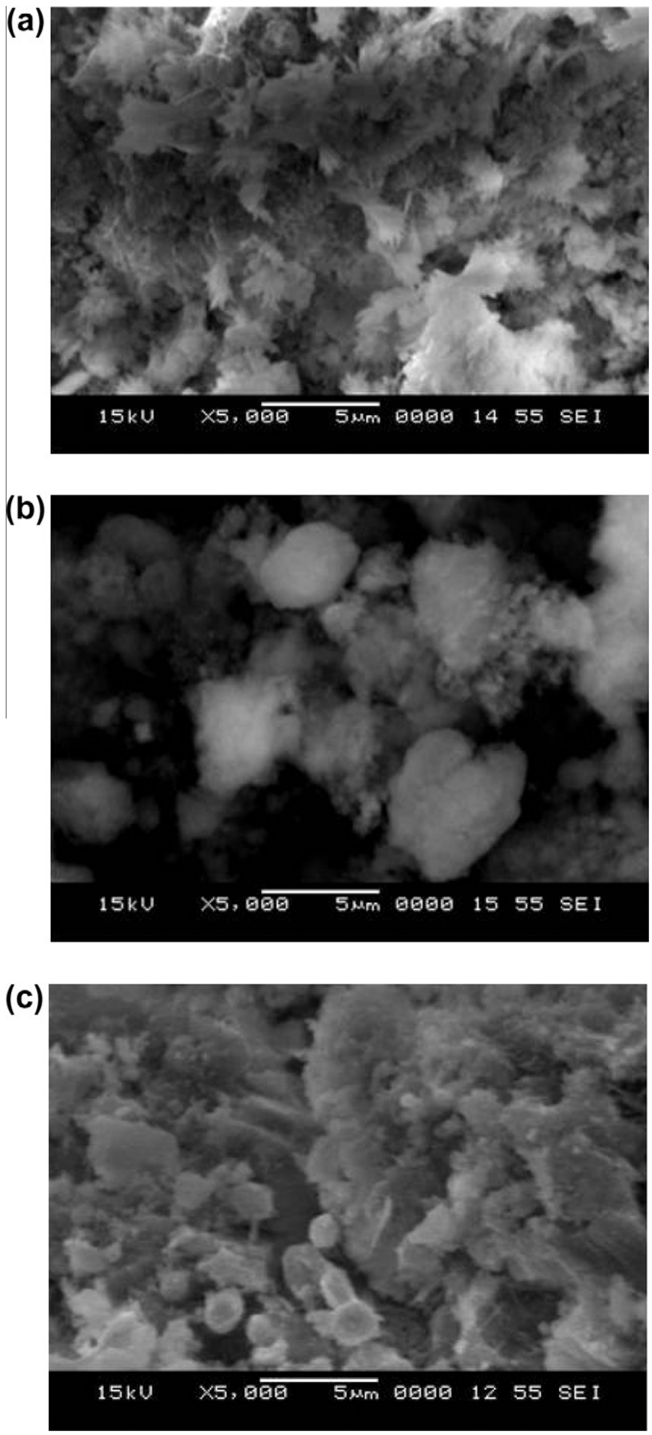

Fig. 5. SEM (a) cured cement, (b) aerogel, and (c) aerogel cement.

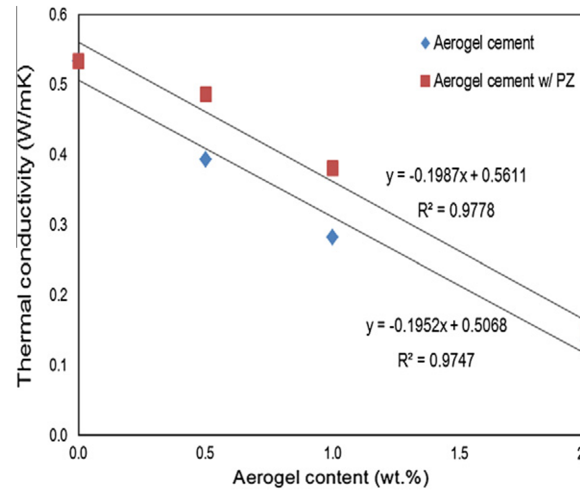

Fig. 6. Thermal conductivity of aerogel cement.

Table 2
Percentages of decrease in thermal conductivity of aerogel cement.

	Aerogel cement				Aerogel cement w/ pozzolan		
Aerogel content (wt.%)	0	0.5	1.0	2.0	0.5	1.0	2.0
Percentages of decrease	–	26.0	47.0	75.0	9.0	29.0	72.0

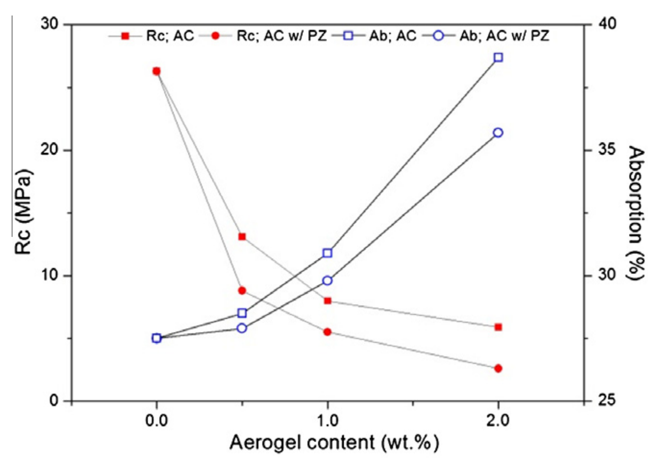

Fig. 7. Relationship between compression strength (R_c, y_1 axis) and absorption (%, y_2 axis) versus aerogel content (wt.%).

more aerogels in the mortar, the compression strength was drastically decreased because the phases change process from gel-typed aerogel to aerogel for curing AC, which was brought about many pores around aerogels. Compression strengths of AC with mass fraction of 0.5, 1.0, 2.0 wt.% were considerably decreased by 50%, 70%, 80% (13.1 MPa, 8.0 MPa, 5.9 MPa) relative to aerogel-free mortar (26.3 MPa). On the other hands, the absorption of AC with that was fairly increased by 4%, 12%, 41% comparing to it. These results showed that the increase of porosity in AC produced by higher aerogel content and yielded the reduction of compression strength. Fig. 8 presents the relationship between flexural strength (R_f) versus aerogel content (wt.%). Decrease in flexural strength was concluded in accordance with mass fraction of 0.5, 1.0, 2.0 wt.% to 33%, 45%, 70% (4.4 MPa, 3.6 MPa, 2.0 MPa) comparing to aerogel-free mortar (6.6 MPa). This is a similar result of the low compressive strength of it. The flow of fresh aerogel mortars is shown Fig. 9. The flow of fresh aerogel mortar was suddenly dropped because methanol used for preparing the gel-typed aerogel absorbed amount of water for mortar mixing process. The flow was sharply decreased from in that case of methanol added, but the amount of aerogel does not have a substantial effect on it.

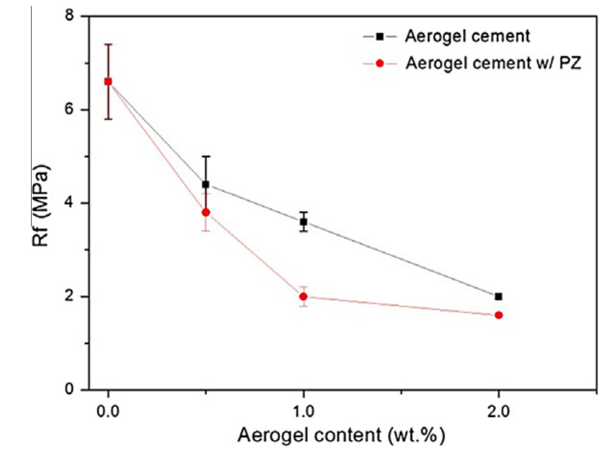

Fig. 8. Relationship between flexural strength (R_f) versus aerogel content (wt.%).

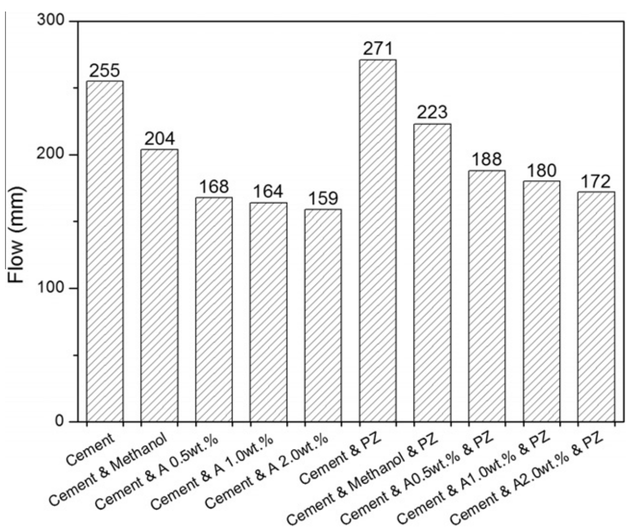

Fig. 9. Flow of fresh aerogel mortar.

4. Conclusions

An experimental study was conducted to determine the possibility of new type of cement composite, the preparing gel-typed aerogel to apply to cement composite and the insulation performance of aerogel cement. Based on the test results, following research findings are derived from this study. Aerogel is very stable material at high temperature by 1150 °C tested by TGA, which indicates that it is possible to apply aerogel to the insulation as well as the building fire-resistance material as a non-structural components. The gel-typed aerogels prepared by methanol were needed in order not only to mix with cement pastes stably, but also to reduce pores between the hydration particle to have the effect on the compression and flexural strength connections of AC. According to FT-IR, there was no chemical molecule change of aerogel on each process; aerogel, gel-typed aerogel and settled aerogel in cement. SEM photo of AC also indicated that aerogels were suitably settled in the cured cement on the process from gel-typed aerogels added process into cement paste to micro physical states of powder-type aerogels. Hence, it was the suitable process to prepare the gel-typed aerogel with methanol for a variety range of aerogel composites because of its very stable characteristics. Thermal conductivity of AC with mass fraction of 2.0 wt.% was decreased by maximum 75% of aerogel-free cement, which means that AC is the cement type performing high insulation to be applicable to an important energy-saving building material. Compression and flexural strength of AC with mass fraction were considerably decreased comparing to aerogel-free cement. On the other hands, the absorption of AC with that was fairly increased in relative to that. This is because the increase of porosity produced by a higher aerogel content yields to a reduction of cement strength. The flow of fresh aerogel cement was drastically decreased because methanol used for preparing the gel-typed aerogel on the process of mixing.

Acknowledgments

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