Microporous calcium silicate thermal insulator

Moulded microporous samples composed of calcium silicates, xonotlite, and tobermorite, were formed by a one-step hydrothermal synthesis reaction. The properties obtained are: 0·131–0·191 kg m^{-3} *density, 0·51–0·90 MN* m^{-2} *compressive strength, 0·25–0·40 MN* m^{-2} *flexural strength, 0·0462* $W m^{-1} K^{-1}$ *(24°C) thermal conductivity, and 1·93% linear shrinkage under firing temperature 800°C for 24 h. The process developed was made possible by the use of accelerating admixtures, which include magnesium acetate and gypsum.* MST/1133

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Introduction

Microporous calcium silicate is one of the best inorganic lightweight thermal insulation materials for high temperatures.[1–32] It is formed by a hydrothermal reaction between SiO_2, from diatomaceous earth,[1] silica fume,[2] fly ash,[3] sludge,[4] zeolite,[5] amorphous SiO_2,[6] etc., and $Ca(OH)_2$ (Refs. 1–5) in a slurry. The reaction results in the formation of tobermorite crystals ($5CaO.65SiO_2.5H_2O$) at about 180°C (Refs. 1, 3–6, 16, 19, 27–29). The mechanism of this reaction involves the formation of calcium silicate gel on the surface of SiO_2 particles, the dispersion of the gel to the slurry, the subsequent adsorption of more $Ca(OH)_2$ crystals on the SiO_2 particles and the repeated dispersion of the gel to the slurry. This continues until the reaction between SiO_2 and $Ca(OH)_2$ is complete. Tobermorite crystals will be formed as the concentration of calcium silicate gel increases. Further heating at or above about 200°C causes the tobermorite crystals to change to xonotlite crystals ($6CaO.6SiO_2.H_2O$) (Refs. 2, 6–15, 17–26, 30, 31). This conversion is accompanied by expansion, as the resulting mixture of xonotlite crystals (needle-like) and tobermorite crystals (plate-like) takes the form of cenospheres (hollow spheres) of a diameter of the order of 10 μm.[17,22] Xonotlite does not degrade up to 1000°C, whereas tobermorite does not degrade up to 650°C.[33]

The hydrothermal synthesis involves heating at or above about 200°C under steam pressure in an autoclave for a few hours. For example, Gliem *et al.*[2] dispersed $Ca(OH)_2$ and silica fume in water at room temperature and autoclaved at 240°C and autogenous pressure (33 bar) for 2–6 h; then, perlite (an acid, igneous, glassy rock of the composition of obsidian) was mixed in and the suspension was compressed and dried at 150°C. This example pertains to a one-step hydrothermal synthesis. In this context, 'one-step' describes the hydrothermal synthesis reaction and does not include mixing, stirring, moulding, cooling, etc. Two-step hydrothermal processes are more common. In one example of a two-step process, the first step involves mixing a slurry comprising milk of lime and SiO_2 powder at CaO/SiO_2 mole ratio of 1 with TiO_2 and water and reacting at 197°C in an autoclave, and the second step involves mixing with alkali-resistant glass fibres and pulp, moulding, and steam curing.[12]

To reduce the cost of the hydrothermal synthesis, it is desirable to have a one-step synthesis and to accelerate the hydrothermal synthesis reaction, thereby decreasing the reaction temperature and/or reaction time. This can be achieved through the use of admixtures. For example, water glass can adjust the alkalinity of the slurry and increase the amount of $Ca(OH)_2$ adsorbed on the surface of SiO_2 particles, thereby making the surface of the SiO_2 particles more active. Bentonite[31,34,35] can generate more gel, thereby increasing the wet volume. In the present paper, in addition to using water glass and bentonite, use is made of magnesium acetate and gypsum, which have not been previously used in this type of hydrothermal reaction. Magnesium acetate can increase the fluidity of the slurry. Gypsum can decrease the size of $Ca(OH)_2$ crystals by 10 to 100 times,[36] thereby making the $Ca(OH)_2$ crystals adsorb on the SiO_2 particles more easily.

Raw materials

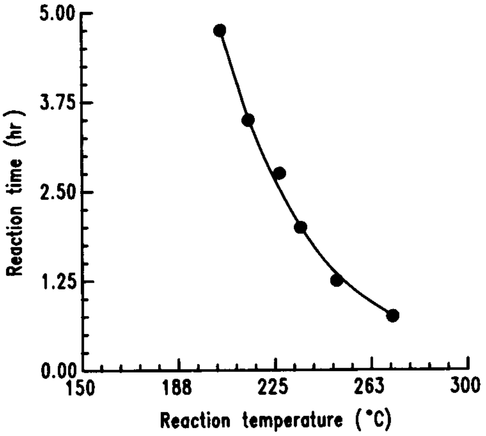
The siliceous material used was diatomaceous earth from Eagle-Picher Industries, Inc., Mineral Division. The calcareous material used was lime from Bellefonte Lime Co., Bellefonte, PA. The chemical compositions are given in Table 1. The water glass used was hydrated sodium silicate which meets Federal Specification O-S-650D Class. However, any other type of water glass can be used instead. The bentonite used was a dry powder, primarily composed of silicon dioxide and aluminium oxide, as provided by NL Brand Western Industries, Inc. Magnesium acetate was used as a chemical agent. Its chemical formula is $Mg(C_2H_3O_2).4H_2O$. The gypsum used was a dry powder, primarily calcium sulphate hemihydrate (β-$CaSO_4.0{\cdot}5H_2O$). It is known as I-C Hemihydrate, as provided by National Gypsum Company. The chemical composition is given in Table 2. Perlite (PERFLO UC216) was used as an aggregate in order to decrease the shrinkage of the moulded body. Its particle size was 0·1–2·5 mm; its bulk density was 0·075 Mg m^{-3}. It was kindly provided by Lomas International Inc. The ceramic fibres used were Fiberfrax Short Staple Fibres from Sohio Engineered Materials Company. The composition and properties are given in Table 3.

Hydrothermal synthesis reaction

A Paar high pressure and high temperature reactor with a stirrer was used as an autoclave to carry out the hydrothermal synthesis reaction. Lime was put into about 5–10 times water and left to stand for more than 1 day until it became a saturated calcium hydroxide suspension (milk of lime). Then diatomaceous earth was put into the milk of lime and more water was added, such that the

Table 1 Chemical compositions of diatomaceous earth and lime, wt-%

Material	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Organics	SO_3
Diatomaceous earth	89·2	0·5	4·0	1·5	0·3	4·0	...
Lime	1·28	94·94	0·28	0·91	0·70	...	0·01



1 Relationship between reaction time and temperature

CaO/SiO_2 mole ratio was 1·07 and the water/solids ratio was 15–20. Then, admixtures, namely, 10 wt-% (by weight of solids) water glass, 1 wt-% (by weight of solids) $MgAc_2$, 10 wt-% (by weight of solids) bentonite, and 5 wt-% (by weight of CaO) gypsum, as well as 7 wt-% (by weight of solids) ceramic fibres, were added to the suspension to give a mixed slurry. The slurry was put into the autoclave, which had a heating rate of about 180 K h^{-1} and a stirring rate of 140 rev min^{-1}. The synthesis reaction was carried out in a saturated steam of 204–271°C for 4·75–0·75 h; the higher the reaction temperature, the shorter the reaction time. The wet volume of the slurry was measured after cooling to room temperature and settling for 24 h.

After the hydrothermal synthesis had been carried out at 227°C for 2·75 h, perlite (15% by weight of solids in the slurry) was mixed into the slurry at room temperature; it was not put in with the rest of the ingredients before the hydrothermal synthesis in order to prevent the slurry from becoming too thick. Subsequently, the mixture was poured into a perforated mould, compressed at 0·9–2·3 Mg m^{-2}, then dried using an oven at about 70°C: the higher the pressure, the higher the density of the resulting material.

Testing methods

According to ASTM C303-82, C165-83, C203-85, and C356-60 (1980), specimens were prepared by using respectively a 51 mm (2in) cubic mould for density measurement and compressive testing and a 40 × 40 160 mm mould for flexural testing (under three-point bending) as well as linear shrinkage and weight loss measurements after soaking heat. The specimens used for testing the compressive and flexural strengths were characterised mechanically using standard methods and a Material Testing System (MTS). According to ASTM C518-85 and ISO3801, specimens were prepared by using a 170 × 170 × 19 mm mould for measuring the thermal conductivity. The k-matic model by Dynatech Scientific Inc. was used for measuring the thermal conductivity at 24°C.

Table 2 Chemical composition of β-$CaSO_4.0{\cdot}5H_2O$, wt-%

Gypsum hemihydrate*	85–90
Gypsum anhydrite	4–6
Calcium carbonate	2–4
Magnesium carbonate	1–2
Free water	Nil
Soluble chloride	<0·01
Acid insolubles	⩽3

*Expressed in terms of gypsum dihydrate (ASTM C471-76).

Table 3 Chemical composition and physical properties of ceramic fibres

Al_2O_3, wt-%	44·0
SiO_2, wt-%	51·0
ZrO_2, wt-%	5·0
Leachable chlorides, ppm	<10
Water of hydration	None
Colour	White
Continuous use limit, °C	1260
Melting point, °C	1790
Fibre diameter, μm	2–3
Fibre length, μm	600–800
Specific gravity	2·62
Fibres, % by weight	42–52

Testing results

RELATIONSHIP BETWEEN REACTION TEMPERATURE AND REACTION TIME

With the wet volume of the slurry after hydrothermal synthesis reaction kept almost constant, the relationship between the reaction temperature and the corresponding required reaction time was investigated. As shown in Fig. 1, the reaction time decreased as the reaction temperature increased.

STRUCTURE

The fracture surface (after flexural testing) of a sample containing no ceramic fibres or perlite particles was examined under a scanning electron microscope (SEM) to study the microstructure of the microporous calcium silicate. Figure 2*a* shows a low magnification image of the cenospheres. In particular, a cenosphere in the lower right quadrant of the photograph is open and it can be seen to be hollow. The cenospheres are typically about 25 μm in diameter. Figures 2*b* and 2*c* show high magnification images revealing the presence of needle-like crystals (xonotlite) that are typically about 3 μm in length and plate-like crystals (tobermorite) that are typically about 2 μm in width. The two types of crystal are intermixed and crosslinked. Between the cenospheres there is a dry gel of hydrated sodium silicate, which results from the water glass remnant.

X-ray diffraction was carried out using Cu $K\alpha$ radiation on a sample containing no ceramic fibres or perlite particles; the presence of xonotlite and tobermorite was revealed.

DENSITY AND STRENGTH

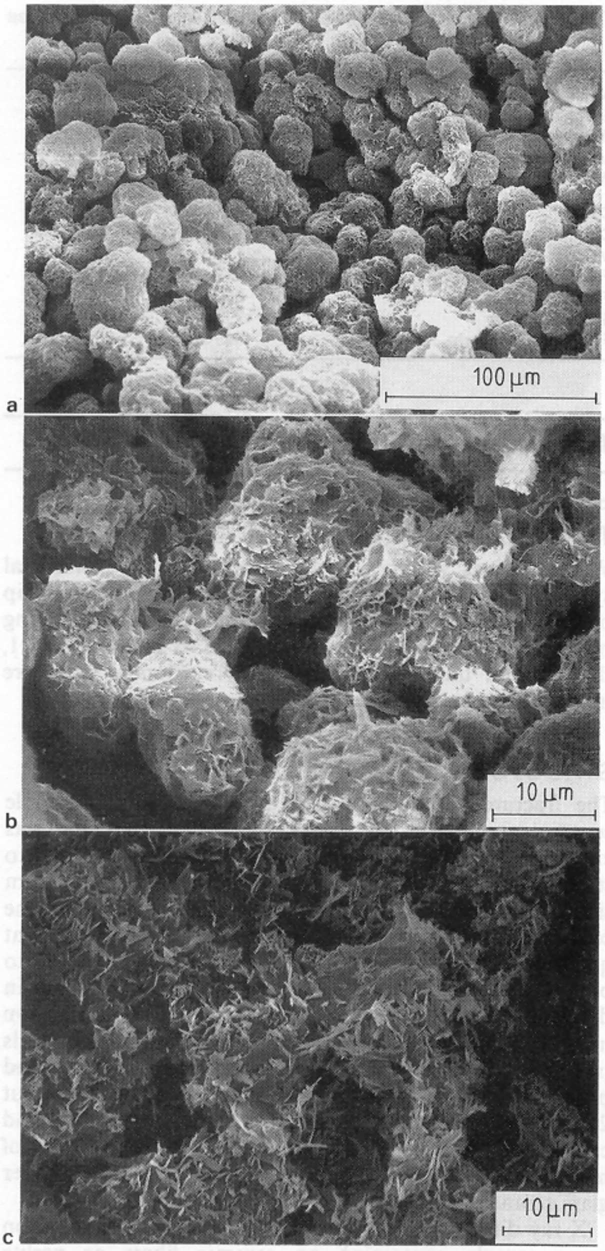
The density, compressive strength, and flexural strength were measured. It can be seen in Table 4 that both types of strength decreased with decreasing density, although not dramatically.

THERMAL STABILITY

Most thermal insulating materials begin to shrink at a certain temperature. The amount of shrinkage increases as the temperature increases. Eventually a temperature is reached at which the shrinkage becomes excessive. When

Table 4 Relationship between density and strength

Density, Mg m^{-3}	0·131	0·164	0·178	0·184	0·191	0·219	0·271
Compressive strength, MN m^{-2}	0·51	0·64	0·87	0·86	0·90	1·29	1·54
Flexural strength, MN m^{-2}	0·25	0·35	0·35	0·40	0·30	...	...

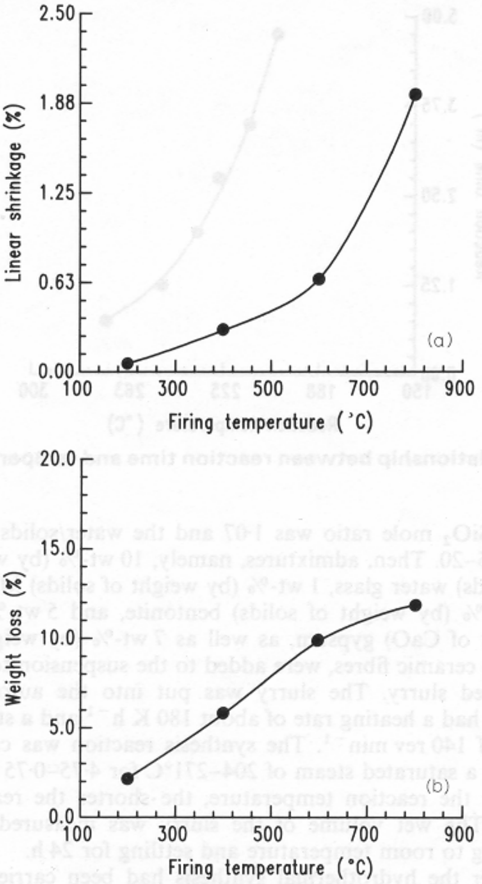


a low magnification of cenospheres; *b, c* high magnification revealing needle-like and plate-like crystals

2 Fracture surface of sample containing no fibre or perlite (SEM)

an insulating material is applied to a hot surface, the shrinkage is greatest on the hot surface. The differential shrinkage which results between the hotter and the cooler surfaces often introduces strain and may cause the insulation to warp. High shrinkage may cause excessive warpage and thereby may induce cracking.[37]

In the present study, the thermal stability of microporous calcium silicate was evaluated by measuring the changes in linear dimensions and weight. Figure 3*a* shows the relationship between the linear shrinkage and the firing temperature; the amount of linear shrinkage increased as the temperature of exposure increased. Figure 3*b* shows the relationship between the weight loss and the firing temperature; the amount of weight loss also increased as the temperature of exposure increased. The linear shrinkage and weight loss were 1·93 and 11·9%, respectively, at 800°C for 24 h. Above 800°C, the shrinkage exceeded the 2% maximum[36] and cracking occurred.



3 Relationship between *a* linear shrinkage and firing temperature and *b* weight loss and firing temperature

THERMAL CONDUCTIVITY

There are three types of heat transfer: conduction, convection, and radiation. When a thermal insulation material has a high porosity, such that the pores are small, closed, and filled with air, it will have a low thermal conductivity, because the thermal conductivity of still air is about $0{\cdot}026\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 300 K. The specific gravities of xonotlite and tobermorite crystals are 2·7 and $2{\cdot}44\ \mathrm{Mg\,m^{-3}}$, respectively. If the density of the microporous calcium silicate specimen is less than $0{\cdot}2\ \mathrm{Mg\,m^{-3}}$ (as it is in this work), the solid volume is less than 8·2% of the whole volume of the moulded body, so there is little heat transfer by conduction. In this study, the microporous calcium silicate was primarily composed of xonotlite and tobermorite crystals agglomerated to form a cenosphere structure (Fig. 2), so the amount of heat transferred by conduction and convection is small. However, during the drying process, much water evaporates, leaving open micropores, which will cause some heat transfer by convection, especially at high temperatures. Heat transfer by radiation will be discussed in the following section.

In this study, the thermal conductivity of the specimen was $0{\cdot}0462\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 24°C for a density of $0{\cdot}152\ \mathrm{Mg\,m^{-3}}$.

Discussion

Making microporous calcium silicate consumes more energy than that required for making many other thermal insulation materials. By using an accelerating admixture, a one-step hydrothermal process for making microporous calcium silicate has been provided. For a reaction temperature of 240°C, the reaction time is 1·75 h (Fig. 1). By contrast, in Ref. 2, for a reaction temperature of 240°C, the reaction time was 2–6 h.

The use of perlite particles as an aggregate is effective for decreasing the shrinkage of the green moulded body, but the heat resistance of normal perlite is less than 800°C. This is why the thermal stability of the present specimens, made using 15% perlite particles, could not reach 1000°C.

For calcium silicate thermal insulation materials, the heat transferred by radiation can be improved by adding infrared shielding materials (e.g. TiO_2, CeO_2, or rutile) to the slurry.[10] Some materials, such as aluminium foils and galvanised iron sheets, can be put on the surface of calcium silicate to decrease the amount of heat transferred by radiation; these materials can also prevent the moisture outside from entering the thermal insulation material.

It is possible to use silica fume, bentonite, and fly ash instead of all or part of the siliceous material to make microporous calcium silicate by using the hydrothermal synthesis reaction, but some reaction parameters require modification.

Using carbon fibres instead of ceramic fibres as a reinforcement is possible. Such a specimen was indeed prepared using pitch-based carbon fibres 3 mm in length (Carboflex of Ashland Petroleum Co.). The thermal conductivity was found to be 0·051 W m^{-1} K^{-1} (24°C) for a density of 0·189 Mg m^{-3}. Because carbon fibres are more expensive than ceramic fibres, the use of ceramic fibres is preferable.

Conclusion

Through the use of accelerating admixtures, a one-step hydrothermal process was developed to make microporous calcium silicate containing xonotlite and tobermorite crystals as main components. The density, the compressive strength, and the flexural strength of the moulded samples were in the ranges 0·131–0·191 Mg m^{-3}, 0·51–0·90 MN m^{-2}, and 0·25–0·40 MN m^{-2}, respectively. The thermal conductivity of the sample having a density of 0·152 Mg m^{-3} was 0·0462 W m^{-1} K^{-1} at 24°C. The maximum service temperature was 800°C.

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