Mineral

A composite thermal insulator based on xonotlite and perlite

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Abstract: A low cost thermal insulating material can be produced by compounding an active xonotlite slurry, fired-perlite, HOMO PAN fibers and glass fibers. The maximum service temperature of the product is 800℃; linear shrinkage after 800℃×16 h firing is 0.9%; the cold crushing strength is 1.56 MPa; the flexural strength at ambient temperature is 0.81 MPa; the thermal conductivity at ambient temperature (25℃) is 0.056 and 0.128 W/(m·K) at 800℃. The production cost of such a composite is only 1/3 of that of the normal xonotlite thermal insulators. It can substitute the normal xonotlite thermal insulators on most occasions with a similar cost to that of normal perlite products.

Key words: perlite; xonotlite; thermal insulator

1 Introduction

It is well acknowledged that fired-perlite has small pores, most of which are smaller than 50 μm [1]. The study results by E. Schlegel, *et al.* [2] suggested that the pore size has enormous effect on the thermal conductivity of the thermal insulating materials, particularly at high-temperatures. Even though perlite products have very low thermal conductivity at ambient temperature, but its thermal conductivity increases rapidly along with the rising of temperature. The reason for this is that there are many inter-grain pores that are much bigger than the inner-grain pores. The sizes of most of these inter-grain pores are between 100 and 1000 μm. A major contribution can be made to both thermal convection and thermal radiation by these big pores at high temperature. In order to reach a lower mass density and a lower thermal conductivity at ambient temperature while keeping a higher cold crushing strength, many products of perlite thermal insulating boards separate fine powders (≤0.15 mm) of its raw materials from coarse grains (≥0.15 mm) [3-4].

The fine powders are put aside for other purposes or completely thrown away. This exacerbates its thermal conductivity at high temperature [5]. With their very low production cost, the fired-perlite boards, shells and other formed products still remain as a kind of major products being used on thermal conducts and walls of furnaces where the maximum service temperature is below 500℃ [6-9]. Therefore the market potential is big in improving the quality both on its thermal conductivity and its service temperature while keeping the production cost as low as possible.

2 Xonotlite slurry as a potential combining agent

Xonotlite-type thermal insulating materials have been used in industry for more than twenty years in Japan and other developed countries [10-13]. They were introduced into China in the late 1980s. Numerous writings and reports about the nature of xonotlite slurry have been accumulated [14-18] both in China and other countries. The xonotlite slurries used in this study were produced with a 10 L autoclave in the Mineral Laboratory of University of Science and Technology Beijing and with a 4 m³ autoclave in Shenze Refractory and Thermal-Insulating Materials Factory (SRTI) for industrial purposes. It is worth noting that even though successful industrial production was achieved based on the data of laboratory experiments, but only in the laboratory the experimental condition can be standardized, the data can be collected in series. So all of the data present in this study are based on the laboratory experiments.

The normal xonotlite slurry (using the same raw

material and the same reaction conditions as that in the industrial production) is dried at 110℃×24 h in the oven, its SEM morphology is shown in **figure 1**. The dried slurry is basically composed of small balls with the diameter of 10-100 μm. These small balls in turn are composed of fiber-like or niddle-like xonotlite crystals, which interconnect to form the balls. The

xonotlite fibers are not evenly distributed in the balls. They are relatively dense around the outside layer of the balls to form a strong shell. Inside the balls, the fibers are loosely distributed to form semi-hollow balls. Thus, the balls usually have very low density, ranging from 0.05 to 0.3 g/cm^3.
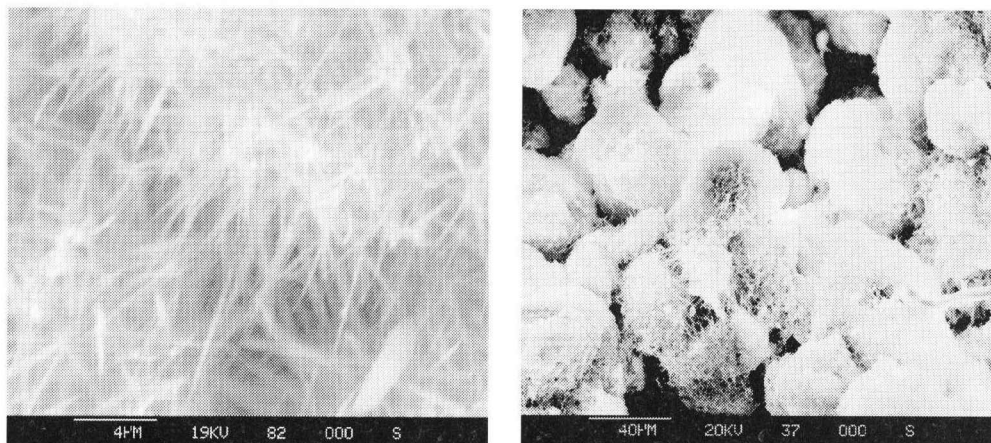

Figure 1   SEM morphology of xonotlite balls.

The diameters of the balls are much smaller than, or in the similar range with that of the inter-grain pores of perlite products mentioned above. So, it is possible to use these xonotlite balls to fill these inter-grain pores of the perlite products, which will largely decrease the thermal conductivity of the perlite products while keeping the bulk density as small as possible.

Apart from the xonotlite balls mentioned above, there still exists a kind of gels in the xonotlite slurry. These gels have similar chemical composition as that of xonotlite (6CaO·6-SiO$_2$·H$_2$O), but have very low crystallinity and nano meter grains. Thus, they have a great surface activity and a complicated electrical charge on their surfaces. Therefore, these gels are very sticky and possessing the properties of combining agent. It is possible that the ratio of gels /xonotlite balls can be adjusted to a proper value by changing the raw material and the reaction condition.

Therefore the xonotlite slurry is a very promising potential combining agent for perlite products. It can hopefully decrease the thermal conductivity of the products, particularly at high temperature. Also hopefully it can rise the service temperature of the products because such a combining agent contains less alkaline metals comparing with the water glass.

3 The preparation of active xonotlite slurry

Five samples of lime and two samples of quartz from different areas were collected as the raw material of the experiments. The lime samples were hydrolyzed to produce lime slurry. The slurry samples were sieved to keep the grain size smaller than 74 μm. The quartz samples were milled and sieved to keep the grain size smaller than 38 μm for quartz 1 and smaller than 15 μm for quartz 2. The results of chemical analysis are shown in **table 1**.

Table 1 Grain sizes and chemical analysis of raw materials for producing xonotlite slurry (mass fraction in %)

Raw materials	Grain sizes / μm	CaO	MgO	Fe$_2$O$_3$	SiO$_2$	Al$_2$O$_3$	others
Lime 1	≤74	90.2	4.6	0.2	2.4	0.3	0.2
Lime 2	≤74	94.6	0.2	0.3	4.2	0.5	0.3
Lime 3	≤74	91.7	6.4	0.1	0.2	0.2	0.7
Lime 4	≤74	96.2	0.5	0.5	1.2	0.4	0.6
Lime 5	≤74	98.2	0.6	0.1	0.4	0.2	0.3
Quartz 1	≤38	0.1	0.1	0.1	99.2	0.4	0.1
Quartz 2	≤15	0.1	0.1	0.2	98.9	0.5	0.2

The five lime samples were mixed with each of the two quartz samples separately to prepare the mixed slurries, which are ready to be used for the autoclaving

reaction. The molecular ratio of CaO/SiO$_2$ is kept at 1 for all of the mixtures. The solid/water ratios of all of the 10 mixed slurries are kept at 1:10. All of the mixed

slurries were autoclaved at 215℃ for 8 h at a continuous disturbed condition. After autoclaving, the mixed slurries became xonotlite slurries that are composed of xonotlite hollow balls and a minor amount of gels. These xonotlite slurries were mixed with fired-perlite grains, and 0.05% (mass fraction) HOMO PAN fibers and 0.1% glass fibers were also mixed with the perlite grains. The HOMO PAN fibers were provided by Hanil Synthetic Fiber Co. Ltd., and the glass fibers were provided by Shenze Refractory and Thermal In-

sulating Materials Factory. After the mixing of fired-perlite, xonotlite slurries and the fibers, the mixture was pressed to expel the extra water, then it was dried at 110℃ for 25 h. Altogether 10 groups of the formed composite samples were prepared corresponding to 10 xonotlite slurry samples. The cold crushing strength, the flexural strength and the linear shrinkage during drying were measured for every group of the samples. The results are shown in **table 2**.

Table 2 Properties of xonotlite-fired perlite composite samples associated with different xonotlite slurries

Item	1	2	3	4	5	6	7	8	9	10
Raw materials	Q 1 L 1	Q 1 L 2	Q 1 L 3	Q 1 L 4	Q 1 L 5	Q 2 L 1	Q 2 L 2	Q 2 L 3	Q 2 L 4	Q 2 L 5
Cold crushing Strength / MPa	0.72	0.82	0.69	1.13	1.24	0.79	0.88	0.71	1.22	1.56
Flexural strength / MPa	0.38	0.43	0.35	0.56	0.71	0.41	0.45	0.38	0.61	0.84
Linear shrinkage after drying / %	0.81	0.72	1.23	1.32	1.45	0.87	0.79	1.33	1.30	1.31
Mass density / $(kg \cdot m^{-3})$	217.2	212.1	220.2	227.1	231.2	219.7	214.5	228.3	221.5	225.4

Note: Q—quartz; L—lime, 1-10—sample number.

The data in table 2 suggest that the strength of the composite samples is enormously affected by the chemical composition of the limes. The general trend is that the higher strength can be obtained when CaO content in the lime is higher. That is, when the xonotlite slurry is used to combine the perlite grains, it is desirable that the natural lime with high purity should be used. When either MgO or SiO_2 is higher in the lime, the resulted composite samples will have lower strength. The data in table 2 also suggest that the finer grains of quartz will contribute to the strength increase of the composite samples. It is shown in table 2 that the samples which use quartz 2 as one of the materials usually have the strength about 10% higher than that of the samples which use quartz 1 as one of the raw materials. So, in the following experiments, lime 5 and quartz 2 were used as the only raw materials to prepare xonotlite slurries.

4 The property change of the composite samples along with the variation of CaO/SiO₂ ratio in xonotlite slurry

Because the theoretical composition of xonotlite is $6CaO \cdot 6SiO_2 \cdot H_2O$, it is therefore a normal way to prepare xonotlite slurries with a molecular ratio of CaO/SiO₂ as 1 when producing xonotlite-type calcium silicate insulating boards. However, in the real autoclaving situation, particularly in the large-scale industrial production, the reacting slurry can never be ab-

solutely evenly reacted, because the mechanical disturbance can never be evenly distributed, in addition to the grain size effect. So in reality, both in laboratory and in industrial production, the slurry containing 100% xonotlite can never be obtained. Our experiences both in laboratory and in industry suggest that in a proper reaction condition, xonotlite dominated slurry can always be formed when the molecular ratio of CaO/SiO₂ is controlled in the range of 0.95-1.05. A general trend is that the stickiness of the xonotlite slurries becomes higher when the CaO/SiO₂ ratio increases. The observation of such slurries with SEM suggests that the higher of the stickiness, the higher content of gels. Besides, the particle sizes of the gels will be finer. In association with this, while the gel content in the xonotlite increases, the content of xonotlite balls will decrease.

When producing perlite-xonotlite composite samples, it is expected that if the slurry containing less gel is used, the strength of the composite sample will be lower. By contrast, if the slurry containing more gel is used, the strength of the composite sample will be higher. But if the slurry contains too much gel or too less xonotlite, the inter-grain pores of perlite grains in the composite samples can not be filled fully. The resulted composite will have higher thermal conductivity and larger drying shrinkage, which will cause the dimension out-of-tolerance or warping.

Table 3 shows the property variation of composite

samples which were prepared by combining perlite grains with active xonotlite slurries that have different molecular ratios of CaO/SiO_2. It is shown that when the slurry has a CaO/SiO_2 ratio of 1.02, the perlite-xonotlite composite has optimum properties.

Table 3 properties variation of composite samples with the change of CaO/SiO_2 ratio of active xonotlite slurries

CaO/SiO_2	Flexural Strength/ MPa	Cold crushing strength/ MPa	Linear shrinkage after drying / %	Linear shrinkage after sintering / % $(800°C \times 16\ h)$	Thermal conductivity at 25°C / $(W \cdot m^{-1} \cdot K^{-1})$	Thermal conductivity at 800°C / $(W \cdot m^{-1} \cdot K^{-1})$	Mass density / $(kg \cdot m^{-3})$
0.96	0.38	0.81	0.7	1.2	0.053	0.131	200.4
0.97	0.42	0.90	0.9	1.2	0.054	0.130	202.1
0.98	0.45	1.02	1.1	1.1	0.056	0.128	205.4
0.99	0.58	1.14	1.2	1.1	0.056	0.126	206.3
1.00	0.63	1.23	1.3	1.1	0.056	0.124	208.2
1.01	0.72	1.37	1.4	0.9	0.056	0.124	209.8
1.02	0.81	1.56	1.5	0.9	0.056	0.128	210.7
1.03	0.83	1.62	2.4	0.9	0.058	0.132	224.3
1.05	0.85	1.67	2.8	0.8	0.060	0.134	231.2
1.05	0.88	1.71	3.2	0.8	0.060	0.136	238.1

5 Discussion

Table 4 is a comparison of properties among the perlite-xonotlite composite, water-glass-combined perlite products and normal xonotlite-type calcium silicate board. It shows that the composite has much lower thermal conductivity (800°C) and higher service temperature than that of the water-glass-combined perlite products. In comparison with normal xonotlite-type calcium silicate board, the composite has similar thermal conductivity both at ambient temperature and at higher temperature. Both cold crushing strength and flexural strength are much higher than that of the xonotlite-type calcium silicate board. But the composite only can be used below 800°C in comparison with the maximum service temperature of 1000°C for the xonotlite-type calcium silicate board.

Table 4   A comparison of properties among the composite products, normal perlite products and xonotlite-type calcium silicate boards

Properties	Normal perlite board (Water-glass-combined)	The composite	Xonotlite-type calcium silicate board
Mass density / $(kg \cdot m^{-3})$	150	210	220
Cold crushing strength / MPa	0.56	1.56	1.02
Flexural strength / MPa	0.31	0.81	0.49
Linear shrinkage after drying / %	0.8	1.5	1.5
Linear shrinkage after sintering / % $(800°C \times 16\ h)$	4.5	0.9	0.4
Thermal conductivity at 25°C / $(W \cdot m^{-1} \cdot K^{-1})$	0.052	0.056	0.056
Thermal conductivity at 800°C / $(W \cdot m^{-1} \cdot K^{-1})$	0.169	0.128	0.128

Note: All data were measured according to GB/T 10699-1998.

A perlite-xonotlite composite, which has a much lower thermal conductivity and higher service temperature than the normal perlite products, can be produced by using highly expanded fired-perlite as major raw materials and xonotlite slurries as combining agent. The reason for such an enormous decrease of thermal conductivity is that the bigger-sized inter-grain pores are filled by the xonotlite balls. These xonotlite balls are semi-hollowed; within them, large amount of micropores of several microns to sub-microns exists. To fill the inter-grain pores of perlite products with such xonotlite balls will not cause an enormous increase of bulk densities of the composites. But it will largely contribute to the strength increase of the composite due to the pore-filling effect. The higher strength of the composite is mainly attributed to such a pore-filling effect and the stickiness of the gels. The dried products of these xonotlite gels are stable both on volume and strength when they are fired below 800°C. It also has no apparent reaction

with perlite grains below such a temperature. Thus, both xonotlite balls and xonotlite gels contribute to the refractoriness of the composite.

In terms of production costs, the perlite-xonotlite composite products are in the similar range of 300-500 ¥/m³ with that of the traditional perlite products. This is only 1/3 cost of the normal xonotlite-type calcium silicate products. It can substitute traditional xonotlite-type materials in many occasions where the maximum service temperature is below 800℃. It has high potentials of application in furnaces, ovens and stoves in the field of metallurgical industry, building materials industry (such as cement production), petrochemical industry and power industry.

6 Conclusions

(1) A perlite-xonotlite composite, which has a much lower thermal conductivity and higher service temperature than the normal perlite products, can be produced by using highly expanded perlite as major raw materials and xonotlite slurries as combining agent.

(2) The high strength and low thermal conductivity of the composite is largely attributed to the pore-filling effect of the xonotlite secondary particles.

(3) The composite has high potentials of application in many sections of industry due to its improved properties and low cost.

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