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METHOD FOR THE PREPARATION OF CALCIUM SILICATE
HYDRATES BY HYDROTHERMAL REACTION AND REFRACTORY
MATERIALS FOR THERMAL INSULATION

The present invention relates to a novel method for the preparation of calcium silicate hydrates by hydrothermal reaction as well as refractory heat-insulating materials composed thereof.

As is well known, various kinds of refractory or heat-resistant materials mainly composed of calcium silicate hydrates are currently on use as a refractory material or as a building material utilizing their excellent performance such as good heat insulation.

The calcium silicate hydrates contained in such materials are in several crystalline forms including, mainly, xonotlite and tobermorites and they are obtained usually by the hydrothermal reaction of a siliceous material and lime in the presence of water under a saturated steam at an elevated temperature.

It is known that the durability in heating of such calcium silicate-based materials largely depends on the crystalline forms of the calcium silicate hydrates. While, when the calcium silicate hydrate initially formed by the hydrothermal reaction is heated, dehydration first takes place leading finally to the transformation to anhydrous calcium silicates via tobermorites and xonotlite. In the process of dehydration and transformation by heating, xonotlite is more stable and consequently can give much better refractory materials than

tobermorites because of the smaller thermal shrinkage of the xonotlite than tobermorites. This is well understood by the heating test of commercially available calcium silicate-based refractory heat-insulating materials indicating that those
5 mainly composed of tobermorites can withstand heating at about 650 °C while those rich in xonotlite withstand heating at 1000 °C or higher.

The starting materials for the hydrothermal reaction, i.e. the siliceous materials and lime, are diversified according to
10 need and availability. The most widely employed siliceous starting materials are exemplified by quartz, siliceous sands, white earth, diatomaceous earth and silica dust.

When highly refractory materials mainly composed of xonotlite are desired, the siliceous starting material should have a
15 content of silica (SiO_2) and a specific surface area as high as possible in consideration of the reactivity. Suitable ones are, for example, finely pulverized quartz, finely divided amorphous silica of volcanic origin, silica dust and fumed or precipitated silica useful as a filler. They have, however,
20 their respective disadvantages from the standpoint of industrialization either in the low availability due to the localized occurrence in the world or in the expensiveness not only by the prices of the material per se but also by the costs for the pulverization into fine powders.

25 Therefore it has been an important problem in the art to develop a novel and economical method for the preparation of calcium silicate hydrates rich in xonotlite and refractory heat-insulating materials mainly composed thereof by use of a starting siliceous material which is outstandingly inexpensive

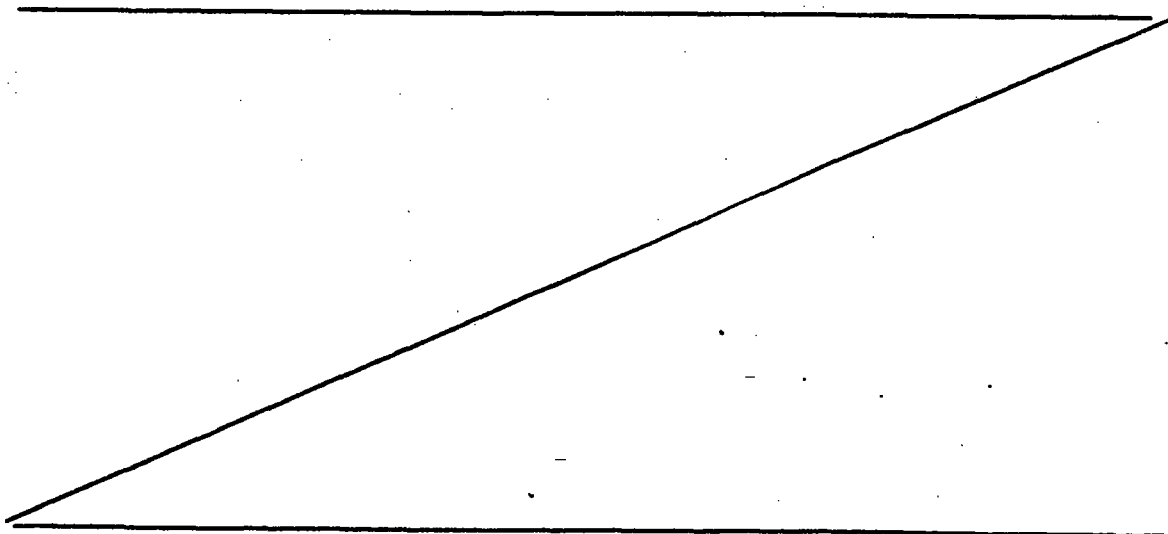
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with good availability but still highly reactive in the hydrothermal reaction with lime. The inventors have accordingly conducted extensive investigations to solve the above problem and have arrived at an idea that the ash from rice husks may be a starting siliceous material suitable for such a purpose since it is known in the botany that the plants of the Gramineae, in particular, rice can collect siliceous constituents from the soil and the siliceous constituents are particularly concentrated in their husks or hulls. The experimental investigations undertaken by the inventors on the basis of the above idea as described below in detail gave unexpectedly satisfactory results leading to the establishment of the present invention.

In one respect, the present invention provides a method for the preparation of a refractory heat-insulating calcium silicate-based material which comprises mixing ash of rice husks and lime in a proportion to give a molar ratio of calcium to silicon in the range from 0.8 to 1.2 together with water to form an aqueous slurry, heating the aqueous slurry under agitation at a temperature of 140°C or higher under a pressure of saturated steam to effect a hydrothermal reaction, yielding calcium silicate hydrate, shaping the thus reacted mixture into a formed body, and drying the thus shaped body.

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In addition to the above mentioned advantages of the invention by the outstanding inexpensiveness and availability of the rice husk ash as well as the excellent performance of the products, an additional advantage is obtained when the heat of combustion of the rice husks into ash is utilized as the heat source for carrying out the hydrothermal reaction and drying of the shaped bodies.

Although the kind of the Granimeae plant from which the husk ash is obtained is not particularly limitative including rice, wheat, barley and rye according to the local availability in the world, it is of course that rice husks are obtained in largest quantities in Japan and the south-eastern Asian areas so that the following description is given almost exclusively with rice husks.

Rice husks are combustible when heated in an oxidizing atmosphere such as air to leave about 20 % by weight of the ash which is useful as the starting siliceous material in the inventive method. The area or district of their growth is not particularly limitative and the husks of the Japanese rice, Indian rice and other sorts of rice are equally suitable. It is a desirable condition that the ashing should be as complete as possible to such an extent that the resultant ash is purely white without any trace of carbon left therein so that the ashing should be conducted under good circulation of the oxidizing gas, e.g. air. The content of silica in a white ash thus obtained may reach 90 % by weight or more depending on

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the sort and area of growth of the rice.

The conditions of ashing are of some importance if not to mention the requirement of the complete ashing as a matter of course. For example, a series of ashing tests were conducted with the same rice husks heated each for 2 hours at a varied temperature between 400 and 1000 °C and the crystalline structure of the silica contained in the ash was examined by the x-ray diffractometry. The results were that the ash obtained at an ashing temperature of 400 to 600 °C is composed of amorphous silica and the amorphous silica in the ash obtained at 800 °C contained a small amount of cristobalite while the ash obtained at 1000 °C was a substantial mixture of the cristobalite and tridymite. In another series of the ashing tests at 800 °C with varied times from 1 to 16 hours, the silica in the ash obtained by 1 hour ashing was amorphous beginning crystallization into cristobalite at about 2 hours from the start and the ashes obtained by heating of 8 to 16 hours were each a substantial mixture of cristobalite and tridymite.

The above results indicate that the silica constituent in the rice husk ash is in the amorphous state when ashed under a milder ashing condition of either a low ashing temperature or short ashing time while increase of the ashing temperature or extension of the ashing time leads to the crystallization of the silica into cristobalite and tridymite as a trend although the crystallization into the more stable crystalline form of quartz hardly takes place. This result is of particular importance since the reactivity of the silica in the amorphous state or in the crystalline form of the

cristobalite or tridymite in the hydrothermal reaction is much higher than the silica in the form of quartz suggesting the superiority of the ash of the rice husks as the starting material for the synthesis of the calcium silicate hydrates by far to the conventional siliceous materials of quartz origin.

It is also noted that the ashed rice husks retain their original form before ashing and have a highly porous and fragile structure with large specific surface areas so that they are very advantageous in the pulverizability into fine ash powder. While the siliceous starting materials used as the starting material for the hydrothermal reaction with lime should be in a powdery form as fine as possible, this feature of the ashed rice husks contributes to a great reduction of the manufacturing costs of the hydrated calcium silicate materials because the costs for the pulverization of the conventional siliceous starting material with low pulverizability constitute a considerable portion of the overall production costs in the prior art.

The other starting material to be hydrothermally reacted with the above described siliceous material is lime to pertain to the reaction in the form of calcium hydroxide. Suitable lime may be quick lime or slaked lime as well as lime-containing materials such as carbide residuum as a waste from calcium carbide-consuming industries.

The preparation of the calcium silicate hydrates to be shaped into the refractory heat-insulating materials according to the invention is carried out by carrying out the hydrothermal reaction with an aqueous suspension or slurry of the finely pulverized rice husk ash and the lime,

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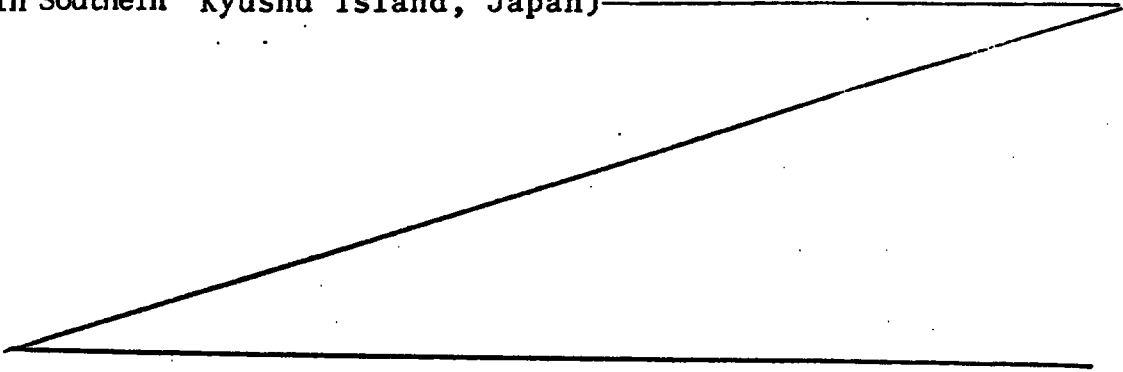
In the above method of carrying out the hydrothermal reaction, the mixing ratio of the rice husk ash and the lime should be such as to give a molar ratio of calcium/silicon (Ca/Si) in the range of from 0.8 to 1.2.

- 5 The optimum mixing ratio of the siliceous material and lime naturally depends on the particle size distribution and the degree of crystallization of the rice husk ash. Higher molar ratios of Ca/Si are preferred when the particle size distribution of the ash is finer
- 10 and when the degree of crystallization of the ash is higher.

It is optional that the mixture of the siliceous material and lime is further blended with various auxiliary materials according to need to obtain desired performance of the refractory heat-insulating materials.

- 15 Such auxiliary materials include conventional siliceous materials and aluminosilicate materials such as pulverized quartz, siliceous sand and clay, reinforcing fibrous materials such as asbestos, rock wool, glass fibers, ceramic fibers, carbon fibers, metal fibers, wood pulp, cotton
- 20 linters and various kinds of synthetic fibers, and light-weight aggregates such as Shirasu (volcanic sand occurring in Southern Kyushu Island, Japan)

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balloons and bloated perlite. These auxiliary materials may be added in combination of two kinds or more.

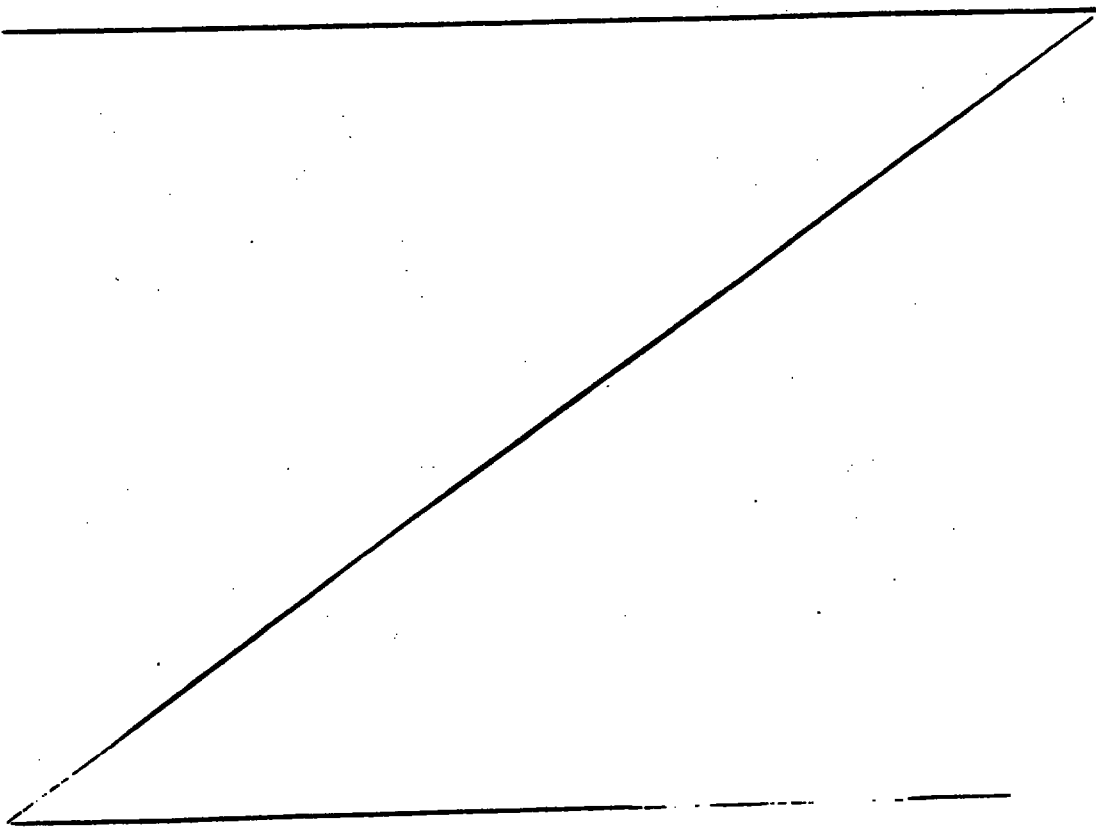
When the hydrothermal reaction is carried out with the aqueous slurry of the starting reactants, the solid content in the slurry should be relatively high in order to obtain well-developed crystals of the calcium silicate hydrates. Though not limitative, the weight ratio of water to the solid matter in the slurry is usually in the range from 5 to 30. The calcium silicate hydrates are formed by heating the aqueous slurry of the reactants at a temperature of 140°C or higher for several hours in a pressurizable reaction vessel such as an autoclave equipped with a stirrer. The reaction temperature should preferably be in the range from 180 to 260 °C when a product rich in xonotlite is desired. The aqueous slurry under the reaction is desirably agitated continuously in order to ensure uniformity of the reaction mixture accelerating the growth of the crystals of the calcium silicate hydrates although it is optional according to desire that the agitation is discontinued at a certain initial stage of the reaction to ensure uniform mixing of the slurry which is subsequently kept standing to grow the crystals under a stationary condition with the stirrer stopped.

The aqueous slurry after completion of the hydrothermal reaction, i.e. the aqueous slurry of the calcium silicate hydrates, is, with optional admixing of the above mentioned auxiliary materials such as the reinforcing fibrous materials

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and light-weight fillers or aggregates according to need, then shaped into a desired form and dried to give a final product of the refractory heat-insulating material. The method for shaping the aqueous slurry into desired forms may be conventional such as casting, compression molding, sheeting or extrusion molding. The moldability of the aqueous slurry may be improved by the addition of certain inorganic materials such as clays and Portland cement (PORTLAND is a Registered Trade Mark) and organic substances such as resin emulsions and water-soluble polymers, e.g. methylcellulose.

It should be noted that the cost of the heat energy is substantial in the method of the preparation of the refractory heat-insulating materials necessary to maintain the temperature of the reactant mixture in a suitable range for the hydrothermal reaction and to dry the shaped body after the



hydrothermal reaction. In this respect, the most advantageous way for obtaining the heat energy with a minimum cost is to utilize the heat of combustion of the rice husks into the ash as the starting siliceous material. The heat of combustion of the rice husks is as large as about 3300 kilocalories per kg of the husks so that full utilization of the heat of combustion of the rice husks greatly contributes to the reduction of the overall manufacturing costs of the refractory heat-insulating materials.

The ash of the rice husks used in the inventive method is an excellent siliceous material with outstanding inexpensiveness and availability in large quantities as well as high reactivity in the hydrothermal reaction with lime along with its pulverizability into fine ash particles to ensure preparation of light-weight refractory heat-insulating materials with low heat conductivity. Further, the advantages of the invention can be increased by the full utilization of the heat of combustion of the rice husks as a heat source required in the process for the hydrothermal reaction and drying along with the possibility of providing a promising means for the disposal of the rice husks as an otherwise burdensome waste material produced in agriculture.

In the following, the method of the present invention is described in further detail by way of examples.

Example 1.

White ash having amorphous structure was obtained by heating rice husks at 600 °C for 15 minutes in an oxidizing atmosphere of air. The ash contained 93.0 % of SiO_2 . After pulverization to have a particle size of 20 μm or smaller, the

ash was mixed with quick lime in a molar ratio of Ca/Si of 1.0. The powdery mixture was slurried in 24 times by weight of water and the aqueous slurry was introduced into an autoclave equipped with an electromagnetically driven stirrer and heated at 190 °C for 8 hours with the stirrer driven at 300 r.p.m. Well-developed needle-like crystals of xonotlite were found in the aqueous slurry after the reaction. The slurry was further admixed with asbestos in an amount of 10 % by weight based on the solids in the slurry as a reinforcing material and molded into a shaped body by press-molding under a pressure of 5 kg/cm² followed by drying at 60 °C. The shaped body of the reaction product had a bulk density of 0.25 g/cm³ and exhibited linear shrinkage by heating of 0.5 %, 0.7 % and 0.7 % when heated for 1 hour at a temperature of 700 °C, 850 °C or 1000 °C, respectively, indicating that the body was an excellent lightweight refractory heat-insulating material with good dimensional stability.

Example 2.

The procedure for the preparation of a shaped body was substantially the same as in Example 1 excepting the omission of the asbestos as a reinforcing material. The thus obtained shaped body after drying at 60 °C was an excellent refractory heat-insulating material having a bulk density of 0.29 g/cm³ and exhibiting linear shrinkages by heating of 0 %, 0.8 % and 0.8 % at 650 °C, 850 °C and 1000 °C, respectively.

Example 3.

The procedure for preparing a shaped body of the calcium silicate hydrates was substantially the same as in Example 1 except that the molding pressure was increased to 20 kg/cm².

The bulk density of the finished body was 0.43 g/cm^3 and the linear shrinkage by heating was 0.6 %, 0.6 % and 0.7 % at a heating temperature of 700 °C, 850 °C and 1000 °C, respectively, indicating that the body was also an excellent refractory heat-insulating material.

Example 4.

The white rice husk ash used in Example 1 was further heated at 800 °C for 1 to 16 hours resulting in the crystallization of the amorphous silica content into cristobalite and tridymite as the heating time was extended. The ash with increased crystallization after longer heating time at 800 °C had poorer pulverizability to give coarser ash particles when the conditions for the pulverization were the same.

Preparation of the shaped bodies of the calcium silicate hydrates was performed with the rice husk ash having different degrees of crystallization after varied heating times in the same manner as in Example 1. The bulk density and linear shrinkage by heating of the shaped body obtained in each preparation are shown in Table 1 below together with the predominant crystalline forms of the heat-treated rice husk ash and the particle size distribution of the pulverized ash as well as the crystalline forms of the calcium silicate hydrates in the products. In the table, the symbols of A, C and T each denote the amorphous form of silica, cristobalite and tridymite, respectively, in the rice husk ash and X and To each denote xonotlite and tobermorites, respectively, as the crystalline forms of the calcium silicate hydrates.

Table 1

Heating time of rice husk ash at 800 °C, hours		1	2	4	8	16
Ash	Predominant crystalline form *)	A	A	A>C	C>A,T	C>T
	Average particle diameter, μm	2-4	2-6	3-9	9-16	6-18
Product	Predominant crystalline form *)	X	X	X>>To	X	X
	Bulk density, g/cm^3	0.28	0.21	0.35	0.39	0.43
	Linear shrinkage, %, at	700 °C	0.2	0	0	0
		850 °C	0.9	0.6	0.1	0.1
		1000 °C	0.9	0.9	0.1	0.5

*) See the text for the definition of the symbols.

Example 5.

Finely pulverized rice husk ash more fully crystallized into cristobalite and tridymite than in Example 4 was mixed with quick lime in varied mixing ratios of Ca/Si by moles in the range from 0.85 to 1.0 and the refractory heat-insulating materials of the calcium silicate hydrates were prepared in the same manner as in Example 1. The crystalline forms of the calcium silicate hydrates, bulk densities and linear shrinkages by heating of these bodies are shown in Table 2. The symbols for the crystalline forms of the calcium silicate hydrates have the same meaning as in Table 1.

Table 2

Ca/Si molar ratio		0.85	0.9	0.95	0.98	1.0
Product						
Predominant crystal-line form *)	To	To	X>To	X>>To	X	
Bulk density, g/cm ³		0.51	0.46	0.34	0.30	0.30
Linear shrinkage, %, at	700 °C	1.5	1.0	0	0	1.1
	850 °C	4.5	1.8	0.5	0.02	2.1
	1000 °C	5.9	3.1	0.5	0.04	2.1

*) See the text for the definition of the symbols.

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CLAIMS:

1. A method for the preparation of a refractory heat-insulating calcium silicate-based material which comprises mixing ash of rice husks and lime in a proportion to give a molar ratio of calcium to silicon in the range of from 0.8 to 1.2 together with water to form an aqueous slurry, heating the aqueous slurry under agitation at a temperature of 140°C or higher under a pressure of saturated steam to effect a hydrothermal reaction, yielding calcium silicate hydrate, shaping the thus reacted mixture into a formed body, and drying the thus shaped body.
2. A method as claimed in Claim 1 wherein the amount of water in the aqueous slurry is in the range of from 5 to 30 times by weight based on the total amount of the ash and the lime.
3. A method as claimed in Claim 1 wherein the heating temperature of the aqueous slurry is in the range of from 180 to 260°C.
4. A method for the preparation of calcium silicate hydrate substantially as hereinbefore described in any one of the Examples.



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5. Calcium silicate hydrate produced by a method as claimed in any one of the preceding Claims.

6. A refractory thermal insulation material comprising
5 calcium silicate hydrate as claimed in claim 5.
