New Microporous Materials for Use in Modern Firing Plants

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Abstract

Heat insulating materials with silicate constituents are widely used in industrial firing systems, in the form of fibre products, bricks and concrete. In a recently completed group project a new type of insulating material was developed on the basis of microporous and high-alumina raw materials. It features excellent thermal insulating properties in high-temperature processes, high thermal shock resistance, resistance to chemical attack, and low shrinkage rates.
The new material made of microporous calcium hexaluminate has been successfully tested in kiln cars in the porcelain industry as well as in the form of wall bricks. The new refractory materials were continuously monitored and studied over a test period lasting over three years. A large part of the materials is still in use today. Particular potential is seen for use of the new material in kilns fired with hydrogen atmospheres at temperatures above 1250°C.

Introduction

Ceramic products undergo thermal treatment in various types of firing plant, such as tunnel, roller, pusher plate and chamber kilns. The maximum working temperatures of the kilns produced by Eisenmann range between 400 and 1800°C.
With a view to lowering both investment and operating costs, particular attention is paid to the thermal insulation in the kiln [8]. Walls, floor and ceiling can be lined with various refractory thermal insulating materials or fibre materials [4, 7]. The working temperature and kiln atmosphere are key factors determining the selection of the materials.
Various aspects must be taken into consideration. The thermal insulation must not only insulate well. Chemical and mechanical requirements are also becoming increasingly important. The ever shorter kiln cycles in fast firing lead to higher concentrations of fluxes, glass formers and volatile constituents in the kiln atmosphere.
In addition, the requirements to be met by the thermal insulation materials are increasing to make provision for the very specific kiln atmospheres used in the firing of technical ceramics.
The physical and chemical properties of commercial products such as lightweight refractory bricks [5] or ceramic fibres (1260°C and 1400°C) for lightweight kiln construction can change as a result of the attack from the kiln atmospheres and may lose their positive characteristics.
This leads to cracks, spalling, shrinkage, hardened and glassy areas, which have a considerable influence on the thermal shock resistance and thermal conductivity of the materials. Particularly in intermittent kiln operation and with varying firing curves, such material changes can cause increased reject rates owing to the contamination of the fired ware by the insulating materials.
The use of more chemically resistant insulation, e.g. made of corundum, improves resistance to the kiln atmosphere, but leads to much poorer thermal insulation and higher investment costs.
These technical challenges and the increasing quality requirements for thermal insulation materials were the focus of the field tests of the newly developed thermal insulating materials. Moreover an alternative to ceramic fibre materials and the small-size lightweight refractory bricks in the ASTM class 30/28 (NF1 and NF2) on the kiln car surface, on walls and in the ceiling is discussed.

Lightweight Thermal Insulation in Ceramic Kiln Construction

The thermal insulation in the walls, floors and ceiling of *Eisenmann* kilns generally consists of low-cost backing insulation to 1000°C and suitable facing insulation, which can consist of several layers. The walls consist of lightweight refractory bricks in the ASTM classes 30, 26 and 23. The backing brickwork consists of various insulating blocks. The facing layers are selected according to chemical, mechanical and thermal criteria.
The wall thickness of the individual layers is defined during the design of the thermal insulation on the basis of heat transfer calculations. It should be noted that the wall thicknesses are not only dependent on the temperature in the kiln chamber and the ambient temperature, but are also influenced by the kiln atmospheres. In hydrogenous kiln atmospheres, thermal insulation decreases. The kiln lining must be adapted accordingly. The kiln pressure can also have an adverse effect on the insulating effect of the thermal insulation layers.
Fig. 2 shows the insulation of an Eisenmann kiln car for a working temperature of 1400°C and a cycle time of 3 hours. In this example, different design alternatives are indicated. The car can be insulated with fibre layers or panels or on the other hand only with fibre panels or in combination with cover plates made of lightweight refractory bricks. The edge areas are lined with precast elements or lightweight refractory bricks.
In the insulation of the kiln cars, particular importance is attached to mechanical strength and thermal shock resistance. This is the only way

Fig. 1
The kiln for the test series: Eisenmann tunnel kiln at Rosenthal in Selb/D

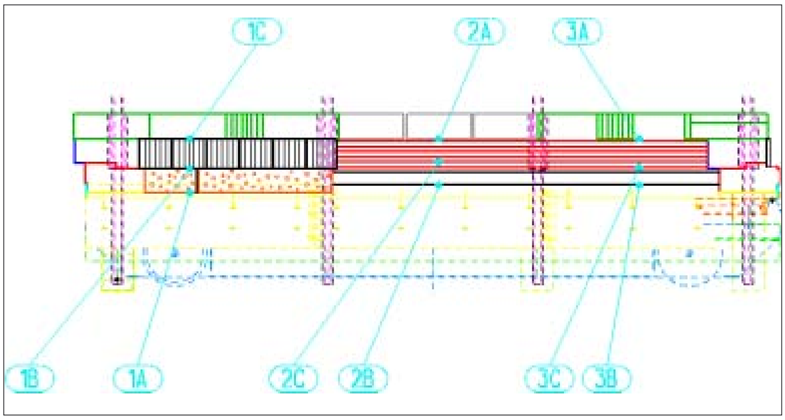

Fig. 2
Different kiln car insulations with their thermocouple measuring points (1A, 1B, 1C bis 3A, 3B, 3C)

to avoid damage that can affect ware being fired. In addition, the thermal storage capacity of the insulation is important to guarantee efficient energy consumption.

Microporous Raw Material SLA-92

The newly developed microporous thermal insulating material SLA-92 (Super Lightweight Aggregate) contains 92 mass % Al_2O_3 and 6...7 % CaO. It has a very low content of impurities, a maximum of 0,1 % for SiO_2 and Fe_2O_3 respectively. The basic mineral composition of SLA-92 is hibonite (calcium hexaaluminate $CaO \cdot {}_6Al_2O_3$, or CA_6). With a melting point above 1830°C, CA_6 exhibits the highest thermal stability of all calcium aluminates. SLA-92 has an apparent density of around 0,75 g/cm³.
The micropore distribution of SLA-92 is shown in Fig. 3. At a total porosity of typically 75 %, the mean pore diameter measures 3...4 µm, with a narrow pore size distribution of 0,5...6 µm. The microporosity of the material is the result of the house-of-cards structure of the CA_6 crystal platelets, which can be seen clearly on the electron microscope image. The spaces between the crystals define the pore size.
This homogeneous microstructure is responsible for two essential properties that distinguish SLA-92 from conventional thermal insulating materials. The small pore diameters impede heat transport by radiation, which, in high temperatures, makes the main contribution to the thermal conductivity of a material. SLA-92 therefore exhibits low thermal conductivity even at temperatures above 1000°C.
Thermal insulation materials are generally prone to spalling when exposed to sudden temperature changes. On account of their low thermal conductivity, a steep temperature gradient is formed in the material, which leads to severe material stresses caused by the differences in expansion rates. These stresses can destroy the thermal insulating materials because, as a result of their comparatively low density, they exhibit only low strength. However, for the material to be destroyed, a stress-induced crack in the material must be able to propagate. In SLA-92, however, this crack propagation is impeded by the microporous house-of-cards structure so that the material has a high thermal shock resistance despite its low density and thermal conductivity.

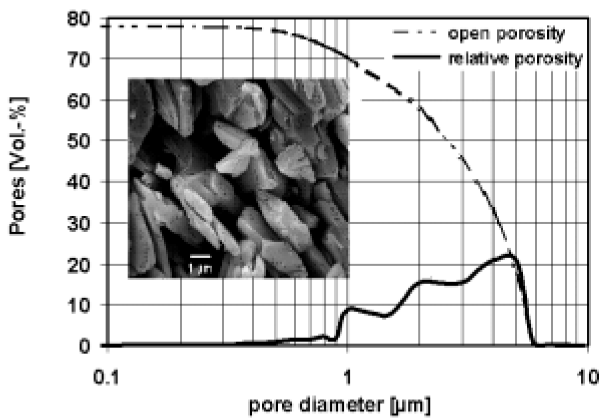

Fig. 3
Microstructure and micropore distribution of SLA-92

Tab. 1
Bond and processing of the refractory thermal insulation materials

Product	Bond	Processing
INTOVAL VL 1000 HT	Hydraulic bond + SiO_2	Casting
INTOVAL Gun VL 1000 HT	Hydraulic bond + SiO_2	Gunning
INTOVAL VL 1000 HT/1	Hydraulic bond + Al_2O_3	Casting
INTOVAL Gun VL 1000 HT/1	Hydraulic bond + Al_2O_3	Gunning

New Microporous Refractory Materials

The "INTOVAL VL 1000 HAT" series is a thermally insulating refractory concrete on the basis of SLA 92.
A total of four new products were developed. As shown in Tab. 1, these materials differ in their raw material composition and processing method.
The gunning product can be used for quick repairs during short kiln stoppages. It can also be applied with a trowel. The casting product on the other hand is designed especially for new linings or the production of pre-cast elements.
In Tab. 2, the high-Al_2O_3 insulating refractory concretes – INTOVAL VL 1000 HT/1 and INTOVAL GUN VL 1000 HT/1 – are compared with lightweight refractory bricks and ceramic fibre materials.
The thermal conductivity of the SiO_2-free series INTOVAL VL 1000 HT/1 is lower than that of the lightweight refractory bricks in the ASTM classes 28 and 30. Above 1000°C it is even lower than that of the ceramic fibre blanket. This can be attributed to the microporosity of the material. With the use of the new insulating refractory concrete, a reduction in the energy consumption can be expected. The strength of the refractory concrete depends on the pre-firing temperature and is on par with that of the lightweight refractory bricks.

Industrial Applications

The industrial application tests were started around four years ago in an Eisenmann tunnel kiln for glost firing porcelain, with a maximum working temperature of 1420°C.
The kiln is fired with natural gas burners and has an oxidizing atmos-

phere up to 1100°C and a reducing kiln atmosphere from that temperature.

To improve melting of the glaze onto the porcelain body, alkalis are added to it as a flux. Part of these alkalis gets into the kiln atmosphere during firing and therefore come into contact with the thermal insulation. This contamination can cause changes in the structure and the properties of the thermal insulation. The cars for this kiln are used for six to seven cycles per day. That works out at a cycle time of three and a half to four hours cold to cold.

The Eisenmann kiln cars are designed with a lightweight refractory brick casing, a fibre core and a complete fibre cover. For the test, two cover plates made of the new microporous material were embedded into the fibre core (Fig. 4). The sample bricks had the dimensions 360 mm x 360 mm x height 100 mm. During the placement of the bricks, it was established that the SiO_2-containing material (3 %) exhibited better dry bending strength and could therefore be mechanically machined better.

In addition, more complex elements were fitted in the corners of the kiln car and around the kiln furniture supports (Fig. 5). A fibre strip module of the type 1430Z was stuck to the surface of some of the bricks. The bottom sides of the new bricks were mortared to the lightweight refractory bricks.

After 700 kiln cycles, a fine network of cracks (Fig. 6) could be seen on the brick surface exposed to the firing atmosphere. The cracks on the SiO_2-containing brick are much more prominent. This network of cracks is formed in a five-millimetre layer on the brick surface so that the actual microstructure of the component does not lose any strength or stability. Even on this cracked surface, it is not possible to detect any spalling or loose particles that could otherwise impair the quality of the fired ware. This underlines the good temperature shock behaviour of the new microporous material.

The more pronounced crack formation on the SiO_2-containing brick is attributed to the sintering effects at the application temperatures. No further tests were conducted with the SiO_2-containing bricks because they have a lower maximum application temperature than the SiO_2-free bricks.

The corner bricks did not exhibit any peculiarities. They demonstrate good adhesion to the fibre adhesive and the lightweight refractory brick mortar. Fig. 7 shows the point of adhesion after the bond had been loosened by mechanical force. The brick structure had to be destroyed to remove the lightweight refractory bricks. The microporous thermal insulation materials can therefore be permanently bonded with other products in thermal insulation systems.

In the following tests, another Eisenmann kiln car (Fig. 8) from a tunnel kiln for firing porcelain was fitted with sample bricks. The test objective was to determine the thermal conductivity, the chemical resistance and the change in the mineralogical phase content of the bricks. The kiln is operated at 1400°C with an alternating oxidizing and reducing kiln atmosphere. The cycles from cold to cold last six and a half to seven hours.

The kiln car insulation was divided into three large zones with different insulation materials and thermocouple measuring points (1A, 1B, 1C bis 3A, 3B, 3C) were attached (Fig. 2). The readings were recorded during ongoing production, although measurement only began after several passages through the kiln to ensure a certain temperature level had been reached in the kiln car insulation. The kiln cycles are only interrupted by short loading and unloading times for the kiln car outside the kiln. In this way, realistic and field-oriented readings could be ensured.

Fig. 9 shows the result of the measurement run with the three different types of insulation. The zone with the cover plates (2A, 2B, 2C) made of the new microporous material enters the kiln with slightly higher starting temperatures owing to its higher heat storage capacity. The maximum temperature reached under the cover plates during passage of the car

Tab. 2 Typical data of insulating materials

	INTOVAL VL 1000 HT/1		Fibre matting		Lightweight refractory bricks	
	CAST	GUN	1430 Z	1600	ASTM 28	ASTM 30
Maximum application temperature [°C]						
	1500	1500	1350	1600	1540	1650
Chemical analysis [%]						
Al_2O_3	89	89	37	80	67	73
SiO_2	< 0,2	< 0,2	48	20	31	25
CaO	10	10	--	--	0,1	--
Fe_2O_3	< 0,5	< 0,5	--	--	0,6	0,5
ZrO_2	--	--	15	--	--	--
Density [kg/m3]						
	1100...1120	1100...1280	128	128	880	1020
Cold compressive strength [MPa]						
	3 - 6	2…6			2,1	2,5
Thermal conductivity [W/mK]						
400 °C	0,30	0,30	0,11	0,09	0,32	0,41
1000 °C	0,28	0,29	0,31	0,28	0,38	0,45
1200 °C	0,36	0,36	0,44	0,41	0,41	0,47

Fig. 4 Large format as an advantage: SiO_2-free and SiO_2-containing sample bricks

Fig. 5 The new material offers complex geometry: cornerstones in the support area

Fig. 6 Hardly any cracks: network of cracks on the SiO_2-containing brick

Fig. 7 Excellent binding: the new microporous refractory material with lightweight refractory bricks

Fig. 8 Kiln car for the glost-firing porcelain kiln

through the kiln is, however, much lower and is reached later than in the fibre modules with a relative density of 160 kg/m³ (1C, 1B, 1A und 3A, 3C, 3B). At the end of the kiln passage, the temperature readings of all thermal insulation types approached one temperature profile.

The measurement results therefore confirm the good thermal insulation properties of the new microporous material in comparison to fibre materials.
After these tests and over 400 kiln cycles, samples were removed for visual, chemical and mineralogical assessment. In this kiln too, alkalis from the glaze attack the thermal insulation. No concentration of alkalis could be detected in the microporous materials. Owing to the effect of the temperature, somewhat higher concentrations of the mineralogical phases gehlenite C_2AS and hibonite CA_6 were determined on the hot face than on the rear of the bricks. Assessed visually, the bricks were in perfect condition (Fig. 10).
Fig. 11 shows another typical application in the critical zone in a stress-relieving roller furnace. The Eisenmann furnace is heated electrically and has an oxidizing firing atmosphere. The wall area shown is exposed to a temperature change of 600°C several times per day, the maximum working temperature reaching 800°C. Besides the thermal shock resistance, in this test a simplified design and assembly was tested. The wall was built with large-size microporous bricks with the dimensions 250 mm x 250 mm and a thickness of 125 mm. Such walls usually consist of several layers of different materials. The photo was taken after seven months of operation and shows a completely intact wall without any damage. Even after 16 months, this wall is still in the same excellent condition.
As a result of the large number of sintering aids added during the firing of ceramic products, different reactive components can get into the firing atmosphere. To estimate their potential effects on the new thermal insulation material, extensive calculations of its thermochemical stability were performed. The conditions considered included:

- Na_2O concentrations up to 5 mass %
- H_2O contents up to 46 %
- oxidizing atmospheres
- atmospheres with 37 % H_2, 6 % CH_4, 5 % CO, 6 % CO_2
- pressures of 1 and 30 bar
- temperatures sometimes > 1600°C.

The results of the calculations showed, for example, that under the influence of Na_2O and with increasing temperature, a small content of ß-alumina can be formed. This coexists with more than 95 % CA phases.
With increasing pressure and in the presence of water vapour, the stability ranges of the CA phases do not change above around 700°C. Below this, slight phase transformations only result in equilibrium conditions.
Reducing atmospheres allow the existence of the stable CA-phases over the entire temperature range.
High temperatures and oxidizing atmospheres do not influence the stability of the calcium hexaaluminate phases.
In the CaO-Al_2O_3 system, only the equilibria shift slightly, the CA_2 and CA_6, however, remain stable.

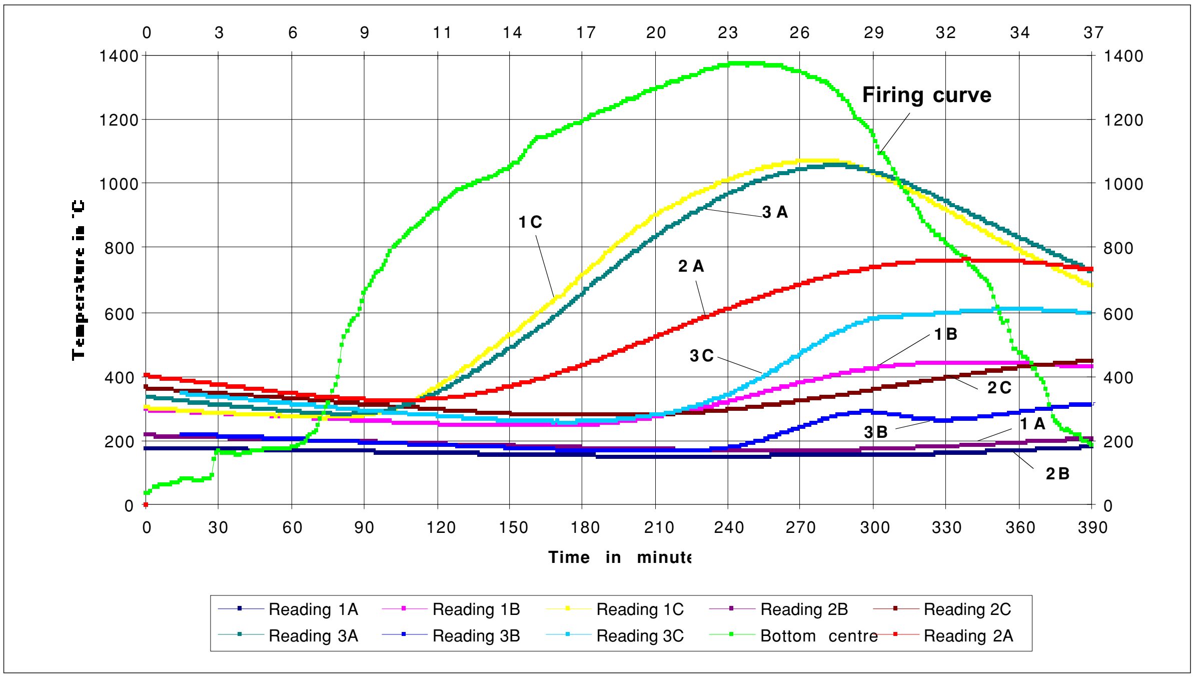

Fig. 9 Temperature readings from a kiln car with different thermal insulation systems

Summary and Prospects

The precast elements and gunning products made of the new microporous calcium hexaaluminate thermal insulation material have a specific density of around 1,1 g/cm³, thermal conductivity between 0,28 and 0,36 W/mK and excellent thermal shock resistance. They can be considered as an effective solution and attractive alternative for insulating critical areas in kilns and furnaces.

Particularly for high-alkali, reducing kiln atmospheres and temperatures between 1300 and 1500°C, the material presents an interesting alternative to corundum bricks with their much higher densities and lower thermal insulation. With the new material, thinner walls are possible.

The excellent thermal shock resistance allows the production of very complex and large-sized components. This simplifies design and helps to reduce installation costs. Moreover, the new material can be used as a gunning and repair compound.

The low thermal conductivity of the microporous material opens up many other possibilities for applications at temperatures above 1400°C. For example, suspended ceilings made of this material with available commercial anchoring systems are also feasible. Improvements could be made at heat bridges in roller feed-through bricks, inspection apertures, burner bricks and viewing ports.

Another aspect is the use of the new material in kilns with a hydrogen atmosphere. For temperatures above 1250°C, these applications require thermal insulation materials free of SiO_2, as otherwise silicic acid reduction can result. This leads to shrinkage and a decrease in strength [2,3].

In an earlier publication, a report was presented on experience gained with the new thermal insulating materials in the steel industry [1,9].

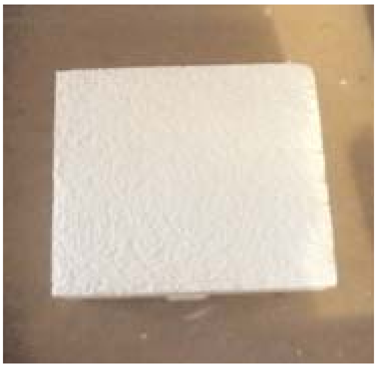

Fig. 10 (left)
In mint condition: microporous brick after over 400 kiln cycles

Fig. 11 (right)
Test passed: wall area of a roller kiln

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