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Kieselguhr sludge from the deep bed filtration of beverages as a source for silicon in the production of calcium silicate bricks

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Abstract

Kieselguhr sludge is generated during the filtration of beverages. Currently, the most frequent disposal method is to spread the used kieselguhr over agricultural land. This is not a satisfactory solution to the problem of disposal. Kieselguhr consists primarily of SiO_2, part of which occurs in the amorphous form.

The goal of this research was to determine whether kieselguhr sludge can be effectively utilized in the fabrication of calcium silicate bricks, and to what extent the kieselguhr sludge plays a role in the reaction mechanisms of the hardening process. Furthermore, the influence of carbonation on calcium silicate bricks produced using kieselguhr sludge was investigated, as well as what effect the preservatives in kieselguhr sludge might have on the entire calcium silicate complex. The laboratory results were subsequently confirmed on an industrial level with a large-scale experiment.

Keywords: Mechanical properties; Strength; SiO_2; Silicate; Waste material; Bricks

1. Suitability of kieselguhr sludge as a source of silicon in calcium silicate bricks

Chapter 1 describes the analysis of the basic technical properties of kieselguhr sludge. This consisted of determining the optimum quantity of kieselguhr sludge to be used as a supplement in the production of calcium silicate bricks, with regard to the strength of the final product and minimizing lime additions during production. Also of interest was whether kieselguhr sludge can function not only as a filler but also as an accessible source of silicon.

1.1. *Kieselguhr and kieselguhr sludge*

Kieselguhr deposits which are currently the focus of mining operations were formed by the sedimentation of siliceous algae (diatoms) during the Tertiary and Quaternary periods.

Kieselguhr mines are found in many parts of the world, including Denmark, Germany, the USA, Russia and China. At present, approximately 1.8 million tons per year are mined worldwide, one third of which originates in the USA. Where kieselguhr has already been discovered, it is estimated that there are at least 900 million tons remaining in these deposits. Mining of this material takes place almost exclusively in open-cast mining operations.[1–4]

Currently, the primary applications of kieselguhr are as a filter aid, as a carrier material as well as a stationary phase for gases and chemicals and as a filler in the construction industry (asphalt). To use it as filter aid it is obligatory to remove impurities, therefore the kieselguhr is subjected to temperatures

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between 600 and 800 °C. At these temperatures, the kieselguhr undergoes calcination as well as a controlled amount of sintering, which coarsens it somewhat. Used kieselguhr must be disposed of or reprocessed. The following work examines whether kieselguhr can serve as a source of silicic acid in the production of calcium silicate bricks.

Approximately 80% of mined kieselguhr is utilized for deep bed filtration. Deep bed filtration is employed for the clarification of media, which are difficult to filter. Filtration of beer is a typical example. In order to achieve the desired level of clarity and stability in the finished beer, all microorganisms and protein particles still in suspension after fermentation and lagering must be removed. These particles immediately cover and therefore block the entire filter surface in vertical flow filters. To circumvent this problem, a highly porous filter aid (kieselguhr) must be added to the beer as it enters the filter. This results in a constant accretion of the filter bed during filtration, which achieves a spatial incorporation of the formerly suspended particles in the filter bed as it accumulates.

A typical kieselguhr dosage ranges between 0.08 and 0.2 kg/m^3. Deep bed filtration is the primary means for filtering beer, juice, wine, spirits, water, gelatin, sugar, citric acid and chemical products. The sludge resulting from filtration, composed of the kieselguhr and the organic substances it contains, is disposed of after filtration has been completed. The current means of disposal on agricultural land cannot be regarded as satisfactory with regard to a sustainable economic cycle.

1.2. Kieselguhr morphology

Kieselguhr particles comprise the former shells of siliceous algae (diatoms) (see Figs. 1–3). They occur in a wide variety of forms, including needle-shaped, round, cuboid, spindle-shaped and elliptical. The surfaces of kieselguhr particles are interspersed with numerous cavities and pores, many of which are only a tenth of a micron in size. Such filigree surface structures result in particles with a small mean particle size which in addition to being a valuable raw material for the construction industry, possess a very large specific surface area; this lies between 1 and 22 m^2/g.[5]

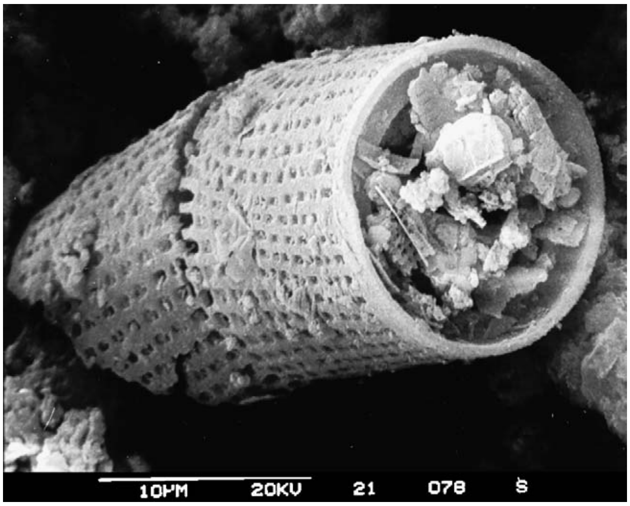

Fig. 2. Scanning electron micrograph of a cylindrical diatom shell, filled with fragments of other diatoms.

Kieselguhr is classified according to its permeability as fine, medium and coarse. Fine kieselguhr enables a more precise filtration but at lower filtration rates. The particle size distributions of typical kieselguhrs are displayed in Fig. 4.[6]

1.3. Chemical composition of kieselguhr and kieselguhr sludge

Kieselguhr varies in its composition depending upon where it originates and what kinds of diatoms it consists of. As with most natural products, the composition of the kieselguhr varies greatly (Table 1).[3]

The mean water content of different types of kieselguhr sludge from filtration of beer amounts to an average 70% by mass. The organic load of kieselguhr sludge varies according

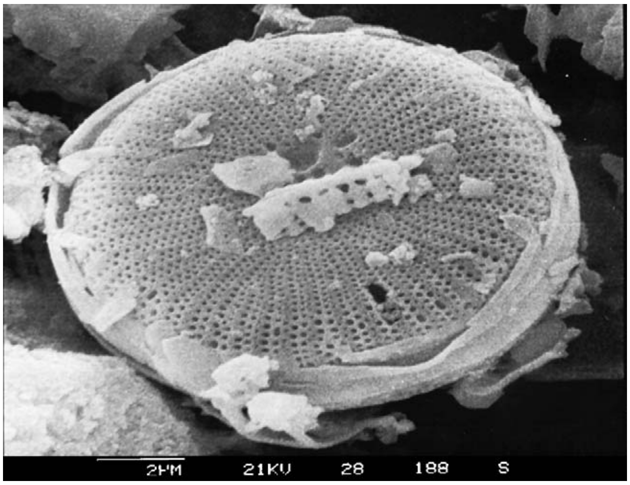

Fig. 1. Scanning electron micrograph of a diatom shell.

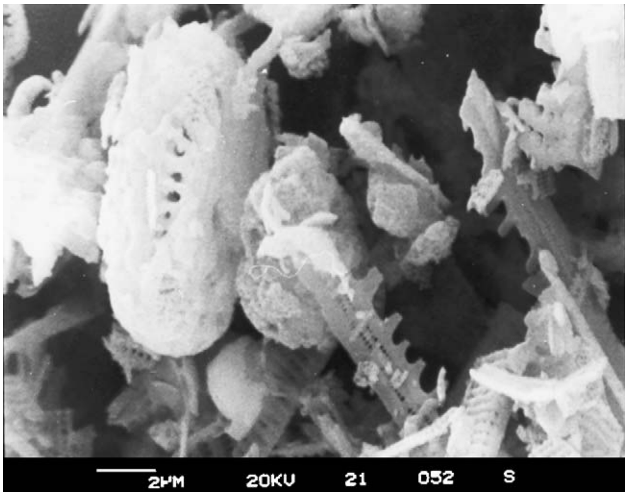

Fig. 3. Scanning electron micrograph of a kieselguhr cluster.

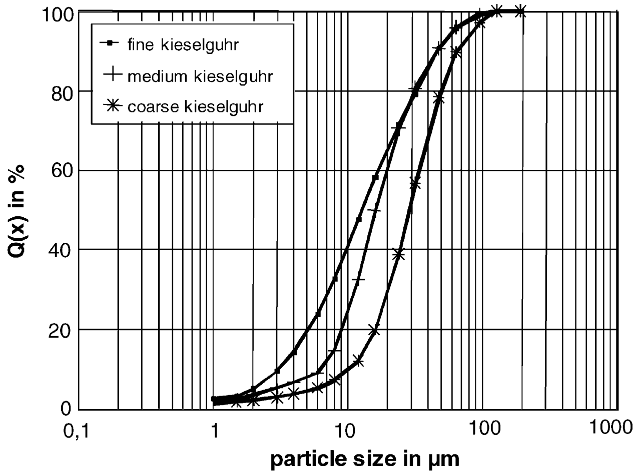

Fig. 4. Particle size distributions of kieselguhr with varying permeability.

Table 1
Mineral composition of kieselguhr used in beer filtration in percentage by mass

Mineral	Percentage by mass
SiO_2	85–91
Al_2O_3	2–5
Fe_2O_3	0.93–10
CaO	0.2–2
TiO_2	<0.2
MgO	0.6–1
Na_2O	0.5–3
K_2O	0.5–3
P_2O_4	<0.1

to the type of beer. The composition of dried kieselguhr sludge is given in Table 2.

The amount of protein and more specifically the nitrogen in the kieselguhr sludge, stems from the yeast cells and protein particles, which were removed during filtration. The measurement of the total glucose content of the kieselguhr sludge also includes the higher molecular weight compounds composed of glucose or starch subunits.

The heavy metal content of kieselguhr was determined using acid hydrolysis followed by atomic absorption spectroscopy (Table 3).

1.4. Other properties

The pH of the kieselguhr sludge is dependent upon the pH of the filtered medium, length of time the kieselguhr sludge was stored and the storage conditions. The values for pH varied from 6.1 to 6.8.

Table 2
Composition of the organic components in dried kieselguhr sludge

	Average value in percentage by mass	Variation in percentage by mass
Raw protein	11.7	8–15
Nitrogen	1.5	0.6–2.3
Total glucose	0.43	
Change in mass	13.2	11.5–13

Table 3
Heavy metal content measured in two kieselguhr sludge samples (measurements in mg/kg of dry mass)

Heavy metal	Sample 1	Sample 2
Nickel	7.43	18
Chrome	7.41	18
Arsenic	0.64	
Mercury	<0.046	0.02
Lead	0.32	2.9
Zinc		32
Cadmium	0.03	0.3

The density of wet kieselguhr sludge varies according to its water content. The density ranges from 1090 to 1160 kg/m^3, with 67 and 71% water by mass, respectively.

1.5. Decomposition during storage of kieselguhr sludge

The organic components in kieselguhr sludge (consisting of trub and other particles) quickly decompose during storage under normal conditions. This decomposition is accompanied by the evolution of strong odors.

1.6. The production process of calcium silicate bricks

Lime and sand are mixed with water, resulting in a mixture with a moisture content of about 8% at the time of pressing. The ratio of lime to sand is approximately 1:10. At this stage, the mixture is pressed into the desired form at a pressure of 190 bar and subsequently autoclaved at a pressure between 6 and 24 bar and a temperature between 160 and 220 °C in a saturated steam environment for several hours. Hardening takes place in the saturated steam environment during which the reaction between the lime (CaO) and silica (SiO_2) produces calcium silicate hydrates (CSH phases, where C = CaO, S = SiO_2 and H = H_2O).

The type of CSH phases and their development influence the characteristics of the calcium silicate bricks. They play an especially crucial role in the strength of the final product.

The formation of the CSH phases takes place in an aqueous solution, and therefore the solubility of the individual components in water heavily influences the formation of new phases.

At room temperature, the solubility of CaO is many times higher than that of SiO_2. At the beginning of the hardening process, excess amounts of calcium are present. On the surface of the quartz particles, small amounts of SiO_2 go into solution and react immediately with the CaO. Through heterogeneous seeding, the CSH phases crystallize.[7–10]

As the hardening process continues, formation of new phases occurs, while others undergo restructuring. The extent of these reactions depends upon the availability of the dissolved ions in the pores. First, the calcium-rich α-C_2SH forms directly on the surface of the quartz, and the crystal formation is localized. The silica is not enveloped by a dense layer. The silica becomes depleted as the α-C_2SH phases continue to develop. As this occurs, crystals with low calcium content, gyrolite ($C_2S_3H_2$) and truscottite ($C_6S_{10}H_3$), can appear.

Almost parallel to the formation of α-C_2SH, the crystallization of CSH-II begins directly on the surface of the quartz. At the beginning of crystallization, the CSH-II structure is very flawed and therefore comes out amorphous when X-rayed. At this stage, the strength of the calcium silicate bricks is still low. As the temperature increases over time, the amorphous nature of the CSH-II experiences a recrystallization, during which the more structured needle-like ondulated to plate ondulated CSH-I appears. This deposits a highly porous layer, maximum 10 μm thick, all over the silicic acid source. Subsequent to this, the reaction occurs only by diffusion. As the Ca^{2+} ions cannot diffuse through the CSH layer, so the silica acid has to diffuse through the CSH layer to reach the lime. At this point, the migration of the silicic acid molecules determines how quickly the reaction progresses. The α-C_2SH and the gyrolite/truscottite, which were initially formed become restructured to form 11-Å tobermorite.

Both the layer facing the silica acid donor as well as the layer facing away from it continue to expand. Initially, a house of cards structure of CSH-I sheets forms on the SiO_2-donor side, which subsequently recrystallizes into hexagonal 11-Å-tobermorite ($C_5S_6H_5$). Concurrently, 11-Å-tobermorite forms on the side where no SiO_2 is present, which is characterized by either a fiber or lath form; depending upon the space available, crystals in several transitional forms to build the final hexagonal tobermorite configuration can appear.

On the side facing the quartz, the tobermorite coarsens, simultaneously expanding into the corroded surface of the quartz, thereby increasing the cohesive strength between the binding agent and the quartz. On the side facing away from the quartz, xonotlite becomes the predominant crystal that is formed into the pores as the hardening process continues. The xonotlite (C_6S_6H) crystals are large and exhibit a typical lath structure but with the points broken off. At this point, the calcium silicate bricks possess a very high strength because of the way the tobermorite crystals are interlocked throughout the structure. The xonotlite does not contribute to the overall strength, because it projects almost entirely into the empty spaces present in the material. On the industrial level, hardening is terminated before xonotlite forms.

As the reaction continues and the remaining free lime is taken up, an excess of silica ions becomes available, which causes a reconfiguration of the existing tobermorite to xonotlite on the side facing away from the silica acid donor. At this point the strength begins to decrease after having reached its peak. On the side facing the silica acid donor, the tobermorite house-of-cards structure continues to coarsen. Further overhardening now leads to a transformation from the previously lime-rich phases to phases containing more silicic acid, which ultimately yields gyrolite. Compared to tobermorite, gyrolite is thicker and exhibits a hexagonal plate structure, which is preferred. Finally, the entire binding medium is transformed into gyrolite, the most thermodynamically stable phase.[8]

When using dolomitic lime, it is believed that the $Ca(OH)_2$ and the $Mg(OH)_2$ substances react separately with the SiO_2, based on the differences in their solubilities.[10] The formation of magnesium silicate hydrates or calcium magnesium silicate hydrates begins only after the reaction rate of $Ca(OH)_2$ with SiO_2 slows as a result of the CSH layer deposits on the quartz particles. These phases contribute to the strength in a similar way that the CSH phases do.

The amorphous form of SiO_2 exhibits a significantly higher solubility than the crystalline form. The solubility is further influenced by particle size, the degree of arrangement and the pH of the solution. An increase in the surface area and imperfections in the arrangement of the silicic acid donor lead to an increase in the solubility of the silicic acid. Kieselguhr represents an amorphous SiO_2 donor composed of fine particles with a large surface area, which is expected to facilitate readily the hardening of a calcium silicate mixture, because a large amount of SiO_2 is quickly available to the system. Generally, if too much crystal seeding occurs, crystal growth can be stunted, thereby hindering the formation of the desired crystalline phases. In instances where space is restricted, however, there is a risk that a gel-type binder might form, which would possess only a low degree of binding power.

1.7. Production of test samples with kieselguhr

A mass ratio of about 1:2 for the amount of kieselguhr sludge to lime was selected for the test samples (Table 4).

The components were mixed in an Eirich mixer for approximately 25 min. Immediately afterwards, the mixture was pressed into blocks with the dimensions 4 cm × 4 cm × 16 cm

Table 4
Composition of the mix of raw material and the sample names used in the test (all values for mass are given in percentage by mass relative to the dry mass)

Sample name	Control samples				Samples containing kieselguhr sludge				
	N2	N3	N4	N5	K1	K2	K3	K4	K5
Lime, dehydrated	3.5	4.6	5.9	9.1	2.3	3.5	3.8	5.9	7.3
Kieselguhr sludge, dehydrated	1.8	2.3	3.0	4.6	1.2	1.8	1.9	3.0	3.7
Sand	86.8	85.1	83.2	78.4	88.6	86.8	86.3	83.2	81.1
Water	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0

Table 5
Particle size distribution of the sand used in the production of test sample blocks containing kieselguhr sludge (Q (*x*) = sieve passage)

Sieve diameter in mm	0	0.063	0.08	0.18	0.25	0.5	1.0
Q (*x*) in percentage by mass	0	0.02	0.07	1.69	5.57	43.99	89.75

Q (*x*) = sieve passage.

using a hydraulic press at 10 MPa for a time period of circa 3 s.

The parameters for the hardening process were as follows:

Temperature	200 °C
Pressure	16 bar
Duration	3.5 h

1.8. Technical analysis of the calcium silicate bricks

Prior to testing, the blocks were conditioned in a drying oven at 50 °C with a relative humidity of 50% until they reached a constant mass.

The following analyses were performed: X-ray diffraction (XRD), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), raw density, water-accessible pore space, BET analysis (specific surface area, porosity), triaxial flexural strength, compressive strength, and shrinkage.

1.9. Laboratory experiments using kieselguhr sludge in calcium silicate bricks

1.9.1. Properties of the raw material used in the production of the test samples containing kieselguhr sludge

Laboratory-grade slaked lime ($Ca(OH)_2$) served as the calcium source.

The particle size distribution of the sand utilized in the experiment is shown in Table 5. The water content of the sand ranged from 1.7 to 3.4% by mass.

The kieselguhr sludge was taken from beer filtration (water content about 90% by mass). It was dried in a drying oven at 50 °C until the water content had reached 51–61% by mass. The mean particle size was 13.6 μm. The specific surface area was 48.7 m^2/g, which was determined using the BET analysis method.

1.9.2. Results of the technical analysis of the calcium silicate bricks containing kieselguhr

1.9.2.1. X-ray diffraction of the test samples containing kieselguhr. Tobermorite, namely CSH-I was detected in all of the samples. In general, the addition of kieselguhr sludge did not cause a change to occur in the composition of the phases nor in the development of the binder in the calcium silicate bricks. The results from the X-ray analysis show also, that the kieselguhr sludge is entirely transformed, although it must be acknowledged that the amount of kieselguhr in its partially crystalline form is relatively small.

1.9.2.2. Thermal analysis of the test samples containing kieselguhr sludge. Thermal analysis confirmed that the calcium hydroxide was entirely converted during hardening in the majority of the samples. Tobermorite was detected in all of the samples and increased with increasing lime content (Table 4). The samples containing kieselguhr sludge had significantly higher amounts of tobermorite than the control samples. It can be inferred from the data that kieselguhr accelerates the hardening of the calcium silicate bricks.

In addition to tobermorite, a portion of the samples also contained various amounts of xonotlite, which indicates that the strength of the samples was approaching the maximum. Organic components from the kieselguhr sludge could not be detected in any of the samples. The organic material in the kieselguhr sludge apparently fully decomposed during the hardening process.

1.9.2.3. Raw density and water-accessible pore space of the test samples containing kieselguhr sludge. The raw density of the freshly made samples increased parallel to an increase in lime content (Fig. 5). The samples containing kieselguhr generally exhibited a noticeably higher raw density.

1.9.2.4. BET analysis of the test samples containing kieselguhr sludge. The results from the BET analysis are summarized in Table 6. The specific surface area and pore volume of the samples were measured by means of adsorption. The

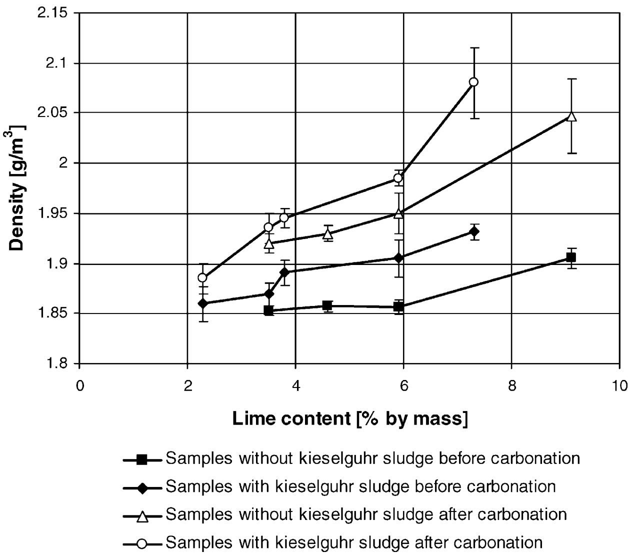

Fig. 5. Raw density of the calcium silicate bricks with and without kieselguhr sludge before (freshly made) and after carbonation.

Table 6
Results from the BET analysis of the test samples containing kieselguhr sludge

Sample	Control	With kieselguhr sludge
Specific surface area (m^2/g)	8.4	15.4
Specific pore volume (mm^3/g)	51	78
Pore diameter (nm)	24.1	20.3

mean pore diameter was then calculated using the values for the specific surface area and the pore volume.

The mean pore diameter was approximately 20 nm for all of the samples, and at this value the surface area and volume distributions each reached their maximum. According to Grundlach, this is characteristic for the CSH phases of the binder in calcium silicate bricks.[10]

A comparison of the samples N4 and K4 shows that the specific surface area was almost doubled through the addition of kieselguhr sludge, which resulted from the increased amounts of fine crystalline tobermorite. For this reason, the pore volume also increased; however, the mean pore size decreased to some extent.

1.9.2.5. Scanning electron microscopy of the test samples containing kieselguhr.

The components present in the binder phase indicate that the hardening process was allowed to reach its maximum strength. The lime content of each sample was closely observed. The binder phase was predominantly composed of tobermorite.

Substituting sand with kieselguhr sludge seems to lead to a strong compression of the structure. The small particle size of both the kieselguhr and the lime facilitated the creation of a homogeneous mixture, which filled in the open spaces of the relatively coarse quartz particles. During hardening a highly porous, fine crystalline binder was formed. Improvements were observed in both the density and strength. The increase in strength changed the modulus of rupture, which partly resulted in the material rupturing into the quartz particles.

In the calcium silicate bricks containing kieselguhr CSH phases formed not only on the quartz particle surfaces but also within the lime–kieselguhr mixture during hardening. Because of this, the reaction rate of the dense CSH-II layer around the sand particles was not slowed. Until the kieselguhr was depleted, diffusion of SiO_2 was only required for very short distances. A further advantage of kieselguhr (amorphous, large surface area) is that its solubility is twice that of sand.

The amorphous structure and the very high specific surface area of the kieselguhr results in a more rapidly available source of silica in the system, and therefore the reaction rate is accelerated. The CSH phases of the samples containing kieselguhr reached a more advanced stage in the hardening process with comparable reaction times.

1.9.2.6. Triaxial flexural strength of the test samples containing kieselguhr sludge.

Fig. 6 shows that the flexural strength of the samples after hardening increased with increasing lime content (calcium hydroxide) of the starting mixture, until the maximum strength was reached. The absolute values were relatively high indicating a good formation of the binder. It has been shown in literature that graphing the strength as a function of the lime content results in a maximum.[9] The strength begins to fall after reaching its maximum despite the continued increase in lime content. According to Gundlach, this is caused by a weakening of the binder resulting from deposits of excess calcium hydroxide.[10]

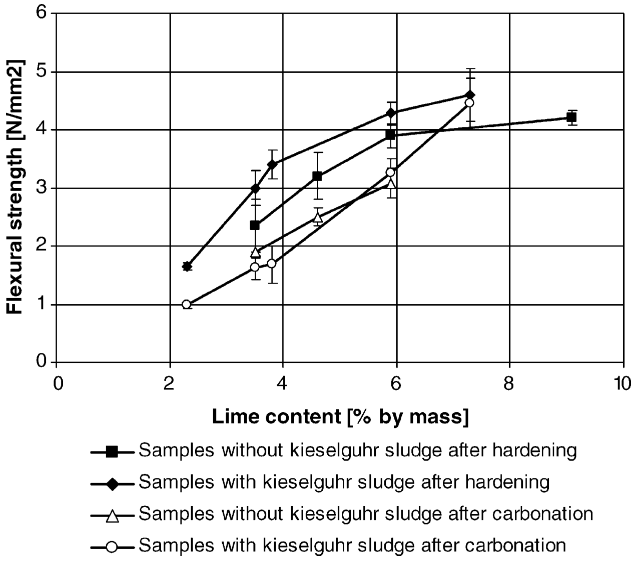

Fig. 6. Triaxial flexural strength of the test samples with and without kieselguhr sludge (after hardening and after carbonation) as a function of calcium hydroxide content.

For the samples after hardening Fig. 6 shows that while keeping the lime content constant the samples containing kieselguhr exhibited an increase in strength of up to 15%. The factors contributing to the higher strength of the samples containing kieselguhr are the same as those discussed above regarding structural analysis.

The results can be interpreted in two ways. An increase in strength was achieved through replacement of the sand with kieselguhr while holding the lime content constant. Additionally, without compromising the strength the amount of lime required in the mixture was able to be reduced with the addition of kieselguhr.

Given the mass ratio of kieselguhr sludge to lime and the information in the figures, it is possible to estimate how much lime can be replaced with kieselguhr without compromising the strength. The samples containing kieselguhr possessed a mass ratio of 1:2, kieselguhr sludge to lime. This means that compared to the samples without kieselguhr sludge, a third of the lime was replaced with kieselguhr.

It is thought that a relationship between the strength and the mass ratio of kieselguhr sludge to lime can be represented by a function with a maximum. Increasing the mass ratio with constant binder content brings about an increase in strength, because the binder structure continues to improve until the maximum is reached. Reducing the lime content further results in fewer CSH phases being formed, which in turn leads to a decrease in strength. It is plausible that the maximum lies within the theoretical Si:Ca mass ratio of tobermorite (4:3).

1.9.2.7. Compressive strength of the test samples containing kieselguhr sludge after hardening. The compressive strength of the test samples was three to five times higher than the flexural strength, which is not uncommon for brittle construction material. In the test for compressive strength, externally induced pressure stresses caused indeterminate shearing forces, which caused material failure by exceeding the tensile strength. For this reason, the flexural strength and compressive strength mirror one another.

The compressive strength and the flexural strength of the samples after hardening exhibit similar dependences (Fig. 7). The strength increases with increasing quantities of lime and kieselguhr. Compared to the control samples, the samples containing kieselguhr sludge displayed not only a 50% increase in strength but also a 50% reduction in the required amount of lime.

1.9.2.8. Shrinkage through loss of moisture in the test samples containing kieselguhr sludge. The degree of shrinkage due loss of moisture measured after 3 months of storage at a constant humidity is presented in Fig. 8.

The degree of shrinkage varied between 0.1 and 0.3 mm/m. For the most part the mean variation in the shrinkage was high. In addition to pure shrinkage due to moisture loss, carbonation reactions take place as a result of the CO_2 present in the air. These reactions are facilitated by the large surface area of the test blocks.

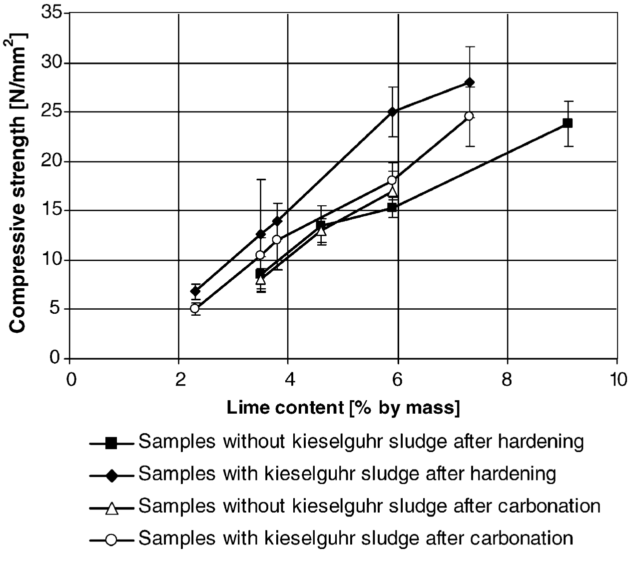

Fig. 7. Compressive strength of the test samples with and without kieselguhr sludge (after hardening and after carbonation) as a function of the calcium hydroxide content.

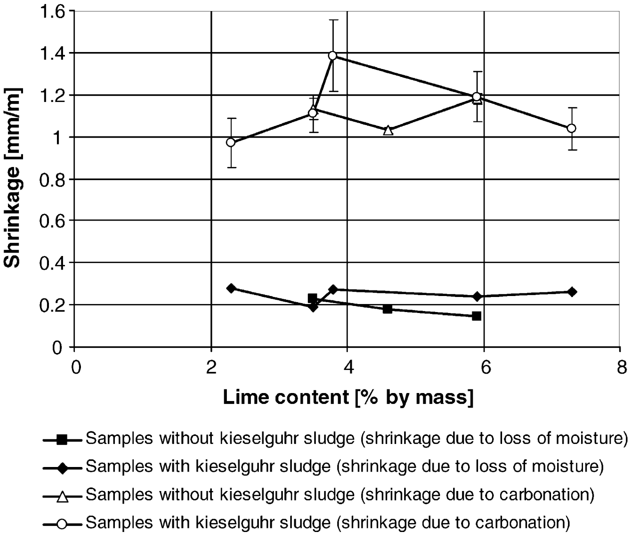

Fig. 8. Shrinkage due to loss of moisture and due to carbonation of the test samples with and without kieselguhr sludge after a 3 months storage period.

1.10. Summary: The suitability of kieselguhr sludge as a silicon source in calcium silicate bricks

On the whole, the utilization of kieselguhr sludge in the production of calcium silicate bricks yielded positive results, which can be attributed to the small particle size, the large specific surface area and the amorphous structure of the kieselguhr. As a result of these characteristics, kieselguhr behaves in the same way as a fine silicate during the hardening process. It dissolves quickly and completely and is converted into binding medium. The organic components in the used kieselguhr decompose during hardening.

Increases in strength and density were achieved through the utilization of kieselguhr sludge. No reduction in flexural strength was observed through decreasing the lime content by up to 40% by mass, and similarly the compressive strength remained constant by reducing the lime additions by up to 50% by mass. The experiments prove that it is possible to utilize kieselguhr sludge in the production of calcium silicate bricks, and that as a result it exhibits significantly better technical properties. Although less lime is needed and hardening requires less time, both of which lower production costs, the quality does not suffer as a result.

A kieselguhr sludge–lime mixture can be successfully integrated into the production of calcium silicate bricks. While still meeting the requirements for raw density and compressive strength, less dehydrated lime or sand is needed for production. This is most evident in the improved particle size distribution of the raw mixture.

Further testing should be done regarding the autoclaving process in order to investigate potential contamination of the condensate through the decomposition of organic components from the kieselguhr sludge, and which measures should be taken in order to ensure compliance with production norms.

2. Influence of carbonation on calcium silicate bricks produced with kieselguhr sludge

This part of the research addresses the carbonation of calcium silicate bricks containing kieselguhr sludge, and whether this process alters its characteristics compared to conventional calcium silicate bricks.

2.1. Carbonation

Carbonation is a reaction between carbon dioxide and construction material containing a CSH binder. Carbon dioxide is present in the atmosphere in a concentration of 350 ppm. Therefore, a reaction between the porous calcium silicate bricks and carbon dioxide is unavoidable.

The carbon dioxide reacts with the CSH phases in the calcium silicate bricks producing calcium carbonate, silica gel and water. This reaction occurs in the liquid phase (the oversimplified formula is given below without regard to reaction stoichiometry).

General formula:

$$CO_2 + C_xS_yH_z \rightarrow CaCO_3 + SiO_2 + H_2O$$

In construction material bound with cement, most notably concrete, gel-type phases form. This means that these binders develop low amounts of crystal formation, and therefore exhibit a tendency for greater shrinkage which makes them susceptible to problems associated with cracking.

In the reaction producing silica gel and water, the properties responsible for the interconnected nature of CSH phases, those which contribute to strength, are lost. The water is released into the surrounding environment, leading to shrinkage. Calcium carbonate ultimately crystallizes to form calcite. This occurs either directly or over the intermediate metastable vaterite, which is a hydrous form of calcium carbonate. It forms more readily in coarse pores as well as on the gaps between quartz particles. The reduction in pore volume through the formation of new phases has two consequences. As a result of shrinkage, the density increases. Furthermore, in the beginning stages of the carbonation, the compressive strength can increase, because the calcite fills and stabilizes the structure.

If the available pores are not large enough to accommodate calcite formation, the structure could rupture. Over time, the strength falls to a minimum; however renewed increase in strength can be attributed to the supporting effect of the calcite.

2.2. Production and carbonation of the test samples with kieselguhr sludge

The production process and the naming scheme used for the test samples were described before.

Before undergoing carbonation, the samples were dried until they reached a constant mass and were subsequently stored in sealed containers in a CO_2 environment at a relative humidity of 63% for 3 months.

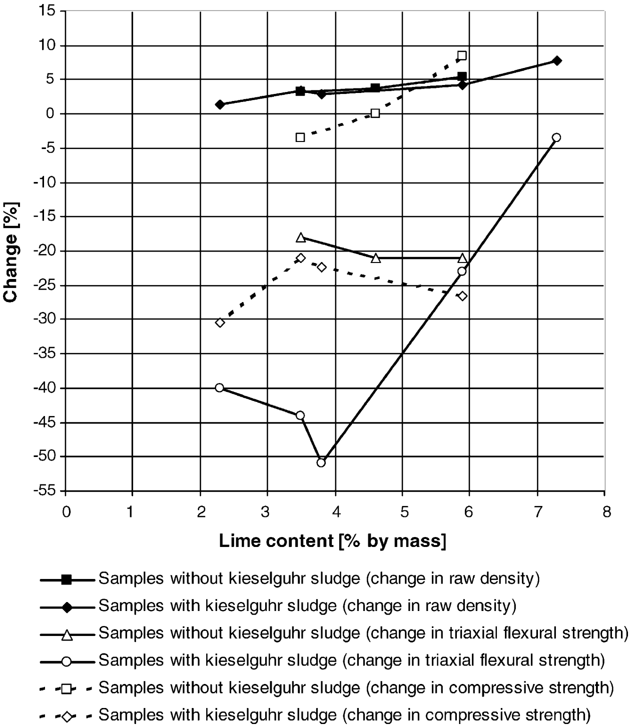

Fig. 9. Change in raw density, triaxial flexural strength and compressive strength as a result of carbonation of the test samples with and without kieselguhr sludge as a function of the calcium hydroxide content.

2.3. Technical analysis of the calcium silicate bricks

Prior to testing, the bricks were conditioned in a drying oven at 50 °C with a relative humidity of 50% until they reached a constant mass.

The analysis included the following: raw density, triaxial flexural strength, compressive strength and shrinkage, as well as scanning electron microscopy (SEM).

2.3.1. Raw density after carbonation

As a result of carbonation, the raw density of all the test samples showed a significant increase, which is illustrated in Figs. 5 and 9.

The increase in density was caused by a reaction between atmospheric CO_2 and the CSH phases, in which the CO_2 was bound as calcium carbonate. Because the CSH phases increase with increasing lime content, the mass also increases proportional to lime content. Therefore, it is evident from the increase in raw density that carbonation reactions occurred to a considerable degree in all the samples.

2.3.2. Triaxial flexural strength of the test samples containing kieselguhr sludge after carbonation

Fig. 6 shows the relationship of the flexural strength to the lime content of the carbonated test samples. The strength increases with increasing amounts of lime and is generally lower compared to the strength of the fresh samples (Fig. 9).

The considerable loss of strength in the samples with kieselguhr sludge is attributable to the decomposition of the CSH phases. After carbonation, the test samples possessed a strength comparable to that of the control samples. This indicates that the phases of the binding medium decomposed to a large extent, thus compromising their strength.

The strength of the control samples showed only a small decrease, because the structure of the binding medium is coarser and more crystalline. The quartz particles are surrounded by a thin CSH layer, which fixes the particles to one another at their points of contact. Where the CSH phases only project through the space of the open pores, they do not contribute to strength. This is largely the case for the control samples, which is why the strength is lower after the hardening process. Only where two quartz particles are bound together with the binding medium, does the decomposition of the CSH phases result in a reduction in strength, which is why the loss in strength is relatively minor. In addition, no rupturing occurs where there is adequate space for calcite formation.

The loss in strength tends to decrease with increasing lime content. Measuring the lime content is a first approach for determining the amount of CSH phases. In the samples containing only a small amount of CSH phases, the CSH phases change completely to calcite, which results in a considerable decrease in strength. At the same time, the CSH phases in the lime-rich samples only partially decompose, and therefore the compromise in strength is more moderate.

2.3.3. *Compressive strength after carbonation*

Fig. 7 shows the compressive strength after carbonation, and Fig. 9, the changes in compressive strength relative to the fresh samples.

The influence of carbonation on the compressive strength is analog to that of flexural strength. The samples containing kieselguhr sludge exhibited a loss in strength (Fig. 9).

2.3.4. *Shrinkage resulting from carbonation of the test samples containing kieselguhr sludge*

Fig. 8 shows the degree of shrinkage caused by carbonation. Ranging from 0.8 to 1.4 mm/m, it is approximately five times higher than shrinkage due to moisture loss, however still under 2 mm/m, the maximum value allowable.

This shrinkage difference is significant, which is very important from a technical standpoint. Values for the samples containing kieselguhr sludge were somewhat higher, because the calcium hydroxide was present as the hydrous pseudomorph vaterite. The water loss from these crystals leads to a higher amount of shrinkage.

The differences in the samples were minute; however the samples containing kieselguhr sludge possessed more CSH phases than the control samples, which resulted in somewhat more shrinkage.

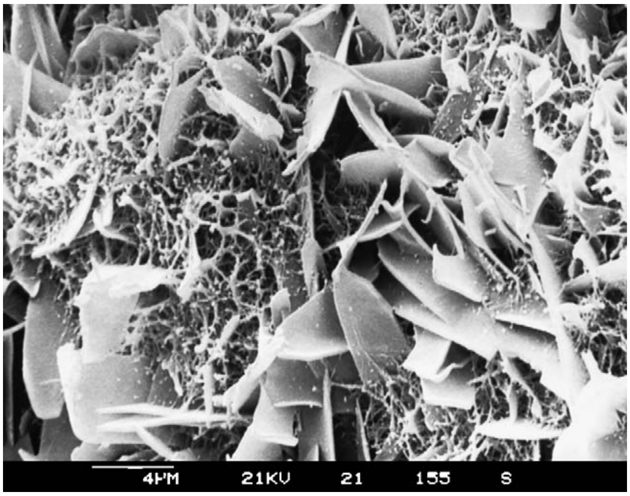

Fig. 10. Silica gel (filigreed structures) and pseudomorphous calcite in carbonated calcium silicate bricks.

2.3.5. *Scanning electron microscopy*

During storage under CO_2, CSH phases are reduced to calcite or to vaterite and silica gel. The calcium carbonate first appears in the pseudomorphous tobermorite lath form (Fig. 10). As the carbonation progresses, the crystals roll together to form rhombohedral structures (Fig. 11). The strength provided by the interlocking nature of the tobermorite crystals gets lost.

2.4. *Summary: The influence of carbonation on calcium silicate bricks made with kieselguhr sludge*

Although all of the samples displayed a significant increase in density through carbonation, the strength of the samples containing kieselguhr sludge fell more sharply than it did in the control samples. Samples with a higher strength before carbonation also tended to display a higher strength after carbonation.

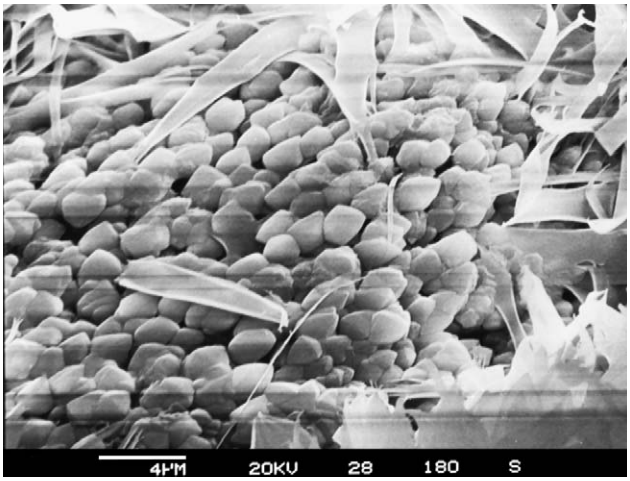

Fig. 11. Transition to rhombohedral calcite in carbonated calcium silicate bricks.

The control samples showed little loss in strength, because the contribution of the CSH phases to their strength was minimal. Additionally, the calcite formation progressed without affecting the structure.

The carbonated samples containing kieselguhr still possessed a similar strength compared to the ones without kieselguhr sludge. In the experiments, a high concentration of carbon dioxide was used to artificially accelerate the aging process, yielding results that would correspond to a storage time of many years. For a normal, non-accelerated carbonation process, one can assume that crack formation caused by the structure rupturing would occur to a lesser extent or not at all, because much more time would be available for these processes to take place.

3. Influence of preservatives in kieselguhr sludge on the quality of calcium silicate bricks

As described in section one, the organic components in the kieselguhr sludge from beverage filtration decompose within a few days through microbial action. Because this process is accompanied by the liberation of very unpleasant odors, preservatives must be added for hygienic reasons, if the kieselguhr sludge is to be used in the production of calcium silicate bricks. The microorganisms responsible for the decomposition must be inactivated. The simplest method of inactivation is to lower the pH below 3 or to raise it above 11.5.

In general, inorganic acids are prohibited for the purpose of lowering the pH in the production of calcium silicate bricks, because through the neutralization reaction with dehydrated lime, salts can form which may later effloresce. It is unclear, however, whether the quantities used to lower the pH would indeed have these effects. Utilizing dehydrated lime to increase the pH in order to suppress microbial activity is described in detail in a publication from the company Uelzener Maschinenfabrik.[11]

Within a few days, the dehydrated lime reacts with the kieselguhr at room temperature to form seed particles for CSH phases. This can only be viewed as positive for the application in the production of calcium silicate bricks. Due to the relatively minor disadvantages associated with this process, such as heat production and the evolution of odors during treatment in the brewery, other preservatives were selected for testing.

Table 7
Composition of the mix of raw material used to make the test samples (all values for mass are given in percentage by mass relative to the dry mass)

Raw material	Control samples	Samples containing kieselguhr sludge
Sand	92	87
Kieselguhr sludge, dehydrated	–	5
Lime, dehydrated	8	8
Water	8	8

The goal of this part of the research was to test the effects of preservatives in kieselguhr sludge on calcium silicate bricks. The water was removed from the kieselguhr sludge before it was used to create the blocks used in the experiment. Standard, commercially available preservatives were chosen for testing.

3.1. Production of the test samples

Production of the test samples was carried out as described in section one above. Table 7 shows the composition of the test samples.

A total of eleven kieselguhr sludge samples, each with a different preservative, were employed in the production of calcium silicate bricks. The preservatives are listed in Table 8. Dry matter is corresponding to samples and to water content of preservatives and cannot be changed without influencing other parameters. Numbers 2 and 3 are not preservatives, but merely serve to mask odors. Additives 4 through 9 are antimicrobial. Sodium benzoate is effective only at a low pH and was therefore added in combination with different organic acids. Additives 10 and 11 increase pH, while alum functions as an anti-microbial as well.

Table 8
Dehydrated kieselguhr sludge samples used in the experiments: concentrations of preservatives and odor-masking substances

No.	Additive		Dry matter in percentage by mass	pH
	Preservative	Concentration in percentage by mass		
1	–		43	7.2
2[a]	Maskomal®	1.0	46	7.1
3[a]	Renosan® 111	1.0	41	7.2
4[a]	P3-Steril KS	1.0	49	6.8
5	copper sulfate	0.5	44	5.0
6[a]	Ammonium tetraformate	1.0	44	3.4
7[a]	Acetic acid/sodium benzoate	0.5/0.01	44	3.8
8[a]	Citric acid/sodium benzoate	0.5/0.1	45	3.4
9	Tartaric acid/sodium benzoate	0.5/0.5	44	3.6
10[a]	Dehydrated lime/alum	1.0/1.0	44	11.3
11	Sodium hydroxide	1.0	41	11.9

[a] Suitable preservatives and odor-masking substances for the addition to kieselguhr sludge to be used in calcium silicate bricks.

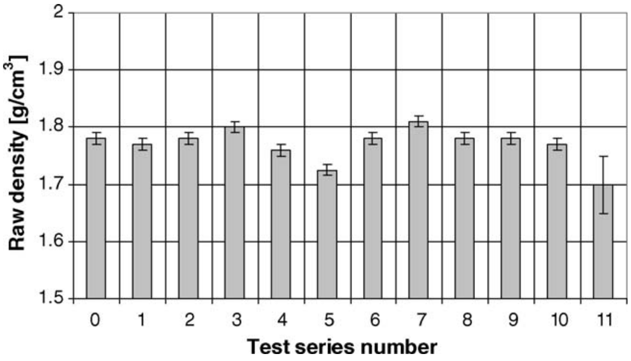

Fig. 12. Raw density of the test samples produced with kieselguhr sludge containing preservatives.

The best preservative qualities were achieved using a combination of an organic acid with sodium benzoate. Dehydrated lime also yielded positive results.

3.2. *Results from testing the technical properties of the calcium silicate bricks*

The determined raw densities of the test samples are given in Fig. 12.

The raw densities of the test series were between 1.70 and 1.81 g/cm^3. The test series containing copper sulfate and sodium hydroxide (numbers 5 and 11) exhibited the most extreme decrease in raw density compared to the control samples, whereas the raw density of the test series with acetic acid/sodium benzoate (number 7) showed a slight increase. The test series containing sodium hydroxide (number 11) displayed a wide range of values for raw density, while the standard deviation of the other test samples was ±0.05 g/cm^3.

The results of the tests for compressive strength are given in Fig. 13. The compressive strength generally increased significantly with the addition of the kieselguhr sludge. Only the test series with copper sulfate (number 5) and sodium hydroxide (number 11) showed a decrease in compressive strength compared to the control samples without kieselguhr sludge. The test series with tartaric acid/sodium benzoate (number 9) experienced a mild reduction of approximately 20% in compressive strength compared to the test series with preservative-free kieselguhr sludge (number 1). However, the mean compressive strength of 18.2 N/mm^2 was still above the 15.5 N/mm^2 of the control sample with no kieselguhr sludge addition (number 0).

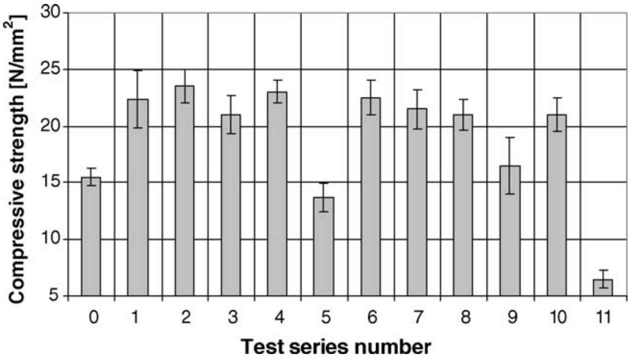

Fig. 13. Compressive strength of the control samples with kieselguhr sludge containing preservatives.

3.3. *Influence of kieselguhr sludge containing preservatives on the technical properties of the calcium silicate bricks*

An addition of 5% kieselguhr sludge, relative to the total dry mass, resulted in only a slight change in the raw density of the calcium silicate bricks. Only the test samples containing sodium hydroxide and copper sulfate showed lower raw densities of 0.08 and 0.05 g/cm^3, respectively, which is attributable to a swelling of the test samples.

The compressive strength of the calcium silicate bricks increased through the addition of the kieselguhr sludge. Negative effects on the compressive strength were evident through increased sulfate or sodium ion concentrations. Especially the addition of copper sulfate and sodium hydroxide resulted in significantly lower values for compressive strength.

The presence of sodium ions causes the formation of double salts, which bind water in their crystal lattice structure, which causes a swelling of the material. The swelling of the test samples was linked to the lower values for raw density, which also resulted in a reduction in their compressive strength.

On average, the compressive strengths of the test samples containing 0.5% tartaric acid and 0.5% sodium benzoate (number 9) as preservatives were higher than the test samples without kieselguhr sludge. Compared to the samples containing kieselguhr sludge without preservatives, the test samples with preservatives exhibited a more pronounced loss in strength. For this reason, the sodium ion concentration should be less than 20 mg/kg.

The presence of sulfate ions also causes the calcium silicate bricks to swell, which results in a considerable loss in compressive strength. Under hydrothermal conditions, sulfates react with the available calcium aluminates to form new crystals ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$ and $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$).

The formation of these new crystals results in a large increase in the volume, therefore ruling out this preservative for use in calcium silicate bricks.

The kieselguhr sludge containing preservatives (at a rate of 5% to the total dry mass), which did not produce negative effects in the technical properties of the calcium silicate bricks, are marked in Table 8.

3.4. *Summary: Influence of kieselguhr sludge containing preservatives on the quality of calcium silicate bricks*

Not all preservatives designed to reduce odors and suppress microbial growth in used kieselguhr are suitable for the production of calcium silicate bricks.

Alkali and sulfate ions in kieselguhr sludge reduce the quality and strength of the finished calcium silicate bricks. Other influences resulting from the addition of preservatives could not be established.

4. Kieselguhr sludge as a raw material for the industrial production of calcium silicate bricks

The laboratory experiments for investigating the use of kieselguhr sludge in the production of calcium silicate bricks were described above. The results from these experiments, however, cannot be directly applied on an industrial scale. Questions regarding processing, mixing and the behaviour of the organic components in the kieselguhr sludge during autoclaving can only be resolved in an industrial setting. Therefore, the goal of this part of the research is to document the results of the large-scale application of kieselguhr sludge and describe its influence on the technical properties of calcium silicate bricks.

The large-scale experiments utilizing kieselguhr sludge containing preservatives were implemented in cooperation with a factory, which produces calcium silicate bricks. The kieselguhr sludge was prepared using dehydrated lime. This method for the inactivation of microorganisms was chosen, as it is the most cost effective option and can readily be used on an industrial scale.

The dehydrated lime functioned well as a preservative when mixed with the kieselguhr sludge, because at the resulting strongly alkaline pH ($\mathrm{pH} > 11.5$) no microorganisms were able to grow. Additionally, the dehydrated lime reacted with the kieselguhr to form CSH seed particles in the mixture, which is beneficial for the production of calcium silicate bricks. The goals of the industrial experiments were to replace dehydrated lime as well as sand with the kieselguhr sludge–lime mixture.

4.1. Preservation of the kieselguhr sludge

The addition of preservatives to the kieselguhr sludge was done in a brewery. The kieselguhr sludge was first collected in a sedimentation tank. The dry substance was approximately 30% by mass. The kieselguhr sludge was prepared in a processing facility by mixing it with dehydrated lime. The mass ratio of the kieselguhr sludge to dehydrated lime was 1:1. A total dry substance of 65% by mass and a bulk density of 600 kg/m^3 were determined for the kieselguhr–lime mixture.

4.2. Production calcium silicate bricks

Calcium silicate bricks were produced in a 3 DF format with a standard raw density of 1.4 g/cm^3.

The composition of the mixtures is given in Fig. 14. Batches I.a and I.b were the regular mixtures used by the industry. Traces of earlier mixtures were found in batches I.a and II.a due to contamination in the mixer. Basalt fragments were added to batch II.a to improve the particle size distribution.

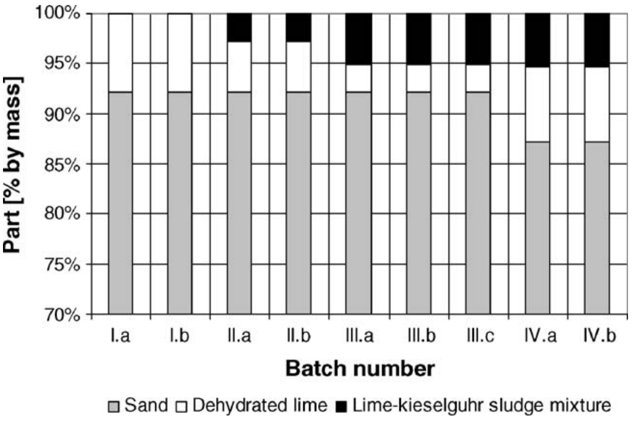

Fig. 14. Composition of the individual batches tested in the large-scale experiment.

The raw materials were mixed with an Eirich mixer, which is commonly used in calcium silicate production. The mixture was held in the reaction tank for 18 h. Pressing was performed at approximately 190 bar of pressure. Autoclaving was done according to the standard industrial method of 1 h of preheating, 6 h at a constant temperature of 200 °C and pressure of 16 bar, followed by 1 h of cooling.

4.3. Analysis of the technical properties

The hardened samples were stored for several weeks in the production warehouse until they reached a constant mass. They were first evaluated through a visual inspection. The density and compressive strength were measured according to DIN 106.[12] Ten individual tests were performed on each batch. From each hardening car, three samples were taken from the upper section, four from the middle and three from the lower section.

The unpleasant odor of ammonia was detected upon opening the autoclave. After a few days, the odor had dissipated from the samples. This odor can be attributed to the hydrolytic decomposition of the proteins. Visually, the samples appeared to be flawless and the color was typical of the high-end products made using pure quartz sand. The edges showed no signs of instability. Inconsistencies and fine cracking were not observed.

The determined raw densities are given in Fig. 15. The raw densities did not vary significantly between the individual batches. The increased raw density of batch II.a was due to a batch of factory sand, which was contaminated with basalt fragments. They also contributed to an increase in the compressive strength. The results of the tests for compressive strength are given in Fig. 16.

There were no significant changes in the compressive strength of the calcium silicate bricks. The increased compressive strength of batch IV.b is primarily the result of its

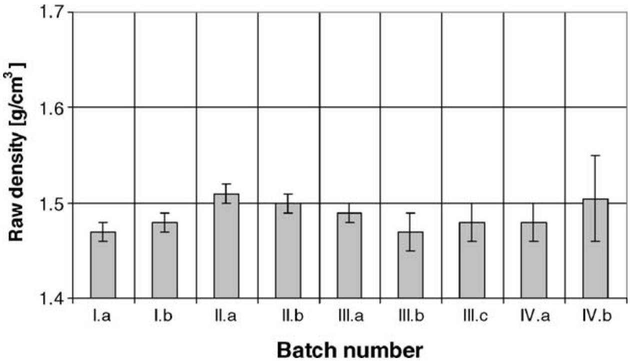

Fig. 15. Raw density of the test samples in the large-scale experiment.

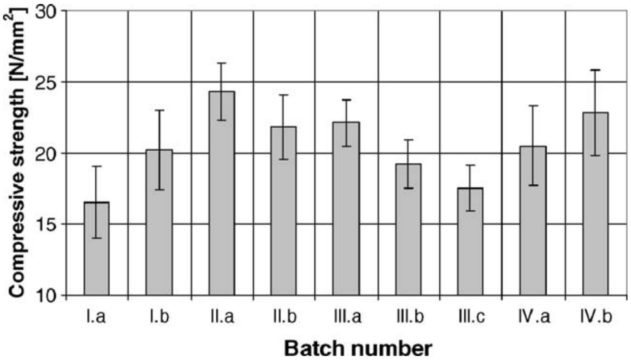

Fig. 16. Compressive strength of the test samples in the large-scale experiment.

increased raw density. Better compression was achieved with this batch using the same pressure.

4.4. Summary: kieselguhr sludge as a raw material in the industrial production of calcium silicate bricks

A mixture of kieselguhr sludge and lime can be successfully incorporated into the production of calcium silicate bricks. Dehydrated lime or sand can be reduced while maintaining the desired standards for raw density and compressive strength. The most obvious result is the improvement of the particle distribution in the raw mixture.

Further experimentation involving the autoclaving process would be necessary to determine what effects the products from the decomposition of the organic components in the kieselguhr sludge would have on the condensate, whether contamination is a threat, and what measures need to be taken in order to ensure that production procedures are in accordance with industry standards.

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