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Influence of the clay type on the pore structure of structural ceramics

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Abstract

The formation of the microstructures of ceramic bodies during firing depending on the clay type will be presented. Through the separation of four different clay types the microstructural development during firing could be systemised. With regard to the hygric behaviour such as capillary suction and humidity absorption as well as to the durability the clay type depending pore structures will be discussed. The influence of the utilisation of industrial wastes in ceramic bodies on their microstructure will be introduced by first results of a current research project and are exemplified by one clay type.

Keywords: Porosity; Wear resistance; Clays; Traditional ceramics; Moisture absorption and capillary suction

1. Introduction

Building materials are characterised by their bulk density, porosity as well as resistance against deformation and mechanical properties, respectively. The weathering resistance can be indirectly assessed by the determination of microstructural parameters.

According to current German and European standards (DIN 105/DIN EN 771-1), the quality, e.g. of facing tiles is specified by their bulk density, water absorption and compressive strength. Furthermore, they have to pass the frost test according to DIN 52252/DIN EN 772-22.

These criteria meet the static requirements for masonry (DIN EN 1053) and general porosity properties. However, they give no information about hygric properties of the materials such as capillary suction or humidity absorption and the resulting potential for damage. In addition, the standard parameters listed do not correlate with hygric and moisture-related properties and the durability, respectively.[1]

As investigations at historical bricks of different temporal and spatial classifications pointed out, the microstructure formed during firing and thus the durability of bricks can only be predicted taking into consideration the impacts of clay types and manufacturing.[9,12–14]

Changes in the mineral phase content, technical and hygric properties and thus the microstructure during firing are significantly affected by the composition of the raw material and by the firing conditions.

In consideration of these aspects and by continuation of associated work[3,4] a classification of clays had been found which makes it possible to derive the hygric behaviour of structural ceramics and to indirectly predict the durability of the materials.

Thus, it will be possible to produce defined microstructures for adequate product qualities, which become more and more important, e.g. for the utilisation of secondary raw materials such as glass or stone wastes in ceramic bodies. By the application of the clay systematisation as well as their combination with the utilisation of secondary raw materials a further improvement of the final product properties with simultaneous energy efficiency could be obtained. That in turn, would lead to a decrease in material inputs and at the same time to an increase in resource productivity which represents a basic contribution to any cost-effective and ecological building.

2. Materials and methods

The investigations comprised 51 clayey raw materials of different geological classifications, which will be exemplified through a characteristic clay of each defined clay type.

Through laboratory tests the development of the microstructure against the clay composition and the firing temperature was determined. Therefore, all raw materials had been sub-

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jected to the same processing. After mixing the powders with water (15–21%) the batches had been aged for 5–8 days for disintegration of the clay minerals. Then, prism-shaped specimens (2.5 cm × 1.0 cm × 12.0 cm) were extruded and dried (100 ± 5 °C) to a constant mass. After firing them in a temperature gradient furnace (3 °C/min, 1 h, free cooling down) the sintering behaviour of these specimens was determined.

Changes in mineralogical and technical/hygric properties of each clay had been investigated from the beginning of microstructural formation to each optimal microstructure covering a temperature range of 400 °C and 200 °C, respectively.

According to current standards, the following measurements had been carried out:[15]

- Porosity
  Water absorption, bulk density, open porosity, density by helium pycnometer (Accu Pyc 1330), true porosity and sealed porosity.
- Pore size distribution by mercury intrusion porosimetry (Autopore II 9220/MICROMERITICS)
  Pore volume, median pore radius according to BENTRUP[5,6,8] $R_{50\%}$, durability ratio according to Maage[7].
- Mechanical properties
  Bending strength

Substantial investigations comprised the texture as well as the chemical and mineral composition which had been determined by the following methods:

- Microstructural images by SEM (HITACHI S 2700 LB/HITACHI)
- Mineral phase content by XRD (D 5000/SIEMENS)

In addition, the amorphous phase content had been analysed with the RIETVELD method (TOPAS R/BRUKER AXS) by using calcium fluoride (fluorspar) as an internal standard.

3. Results and discussion

3.1. Classification of clay types

The silicate formation process and thus the formation of characteristic mineral phases and microstructures are influenced by the mineral content of the raw material, which depends on their local geological sources. In natural clays there are variable compositions of mineral phases, mainly of their plastic components such as clay minerals with different lattice structure and behaviour.

The classification of the raw materials based on the determination of the mineral phase contents by XRD of both the total sample (<63 μm) and the mineral size fractions of <2 μm and <6.3 μm, which had been gained by sedimentation. Afterwards, the clays were classified by defining the ratio of muscovite + illite/kaolinite/alternating strata minerals + smectite.

Furthermore, the amount of earth alkali carbonates was calculated from the analysed contents of CO_2 as $CaCO_3$.

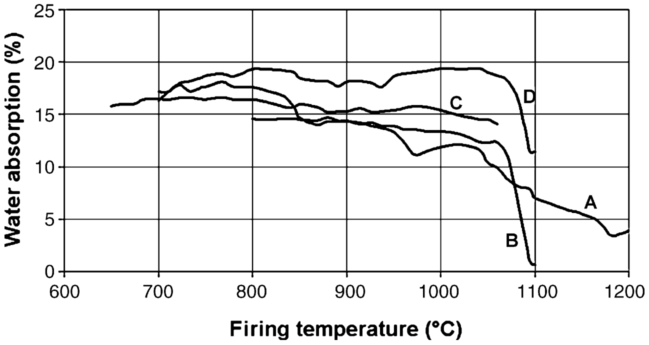

Fig. 1. Water absorption against the firing temperature of the four clay types.

The amounts of grogging components such as quartz- and feldspar-, iron-containing minerals and not mentioned clay minerals of the raw materials as well as the degree of the clay mineral lattice disorder are not displayed. Although they influence the sintering behaviour and the process of microstructure formation they are only partly taken into consideration when commenting on the results.[2,10,11]

The following four clay types are distinguished:

A. Kaolinitic clays mostly containing kaolinite
B. Illitic-kaolinitic clays mostly containing mica/illite
C. Mixed-layer clays containing expandable clay minerals (alternating strata minerals, smectite, three-layer minerals)
D. Carbonate-containing clays with amounts of carbonates (calcite and dolomite) >9%

3.2. Sintering behaviour

The clays can be classified by analysing the formation of the microstructures and the development of properties during firing, especially the pore size distribution as an indicator for the hygric behaviour of the final products (Figs. 1 and 2). The characteristical examples of the four clay types display different amounts of capillary-active and sorption-active pores. The following paragraphs comment on the dependence of the microstructural formation on the clay type during firing which makes it possible to indirectly predict the durability by means of pore radius criteria.

The *kaolinitic clay type A* (CT A) shows dens microstructures (water absorption <5%) at optimal firing temperatures and

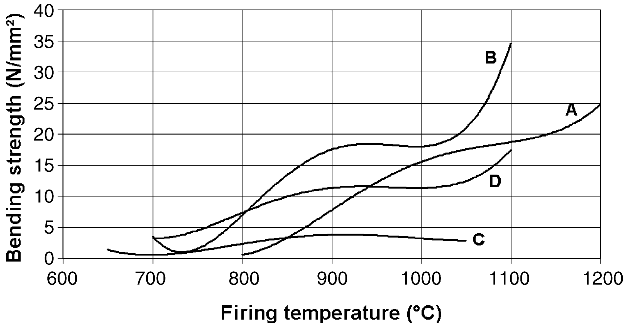

Fig. 2. Bending strength against the firing temperature of the four clay types.

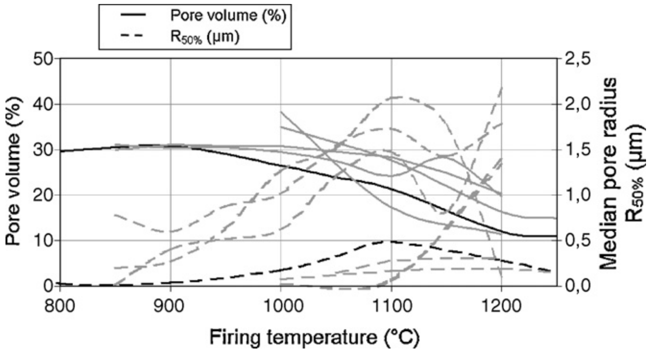

Fig. 3. Development of the pore volume and the median pore radius $R_{50\%}$ of clay type A.

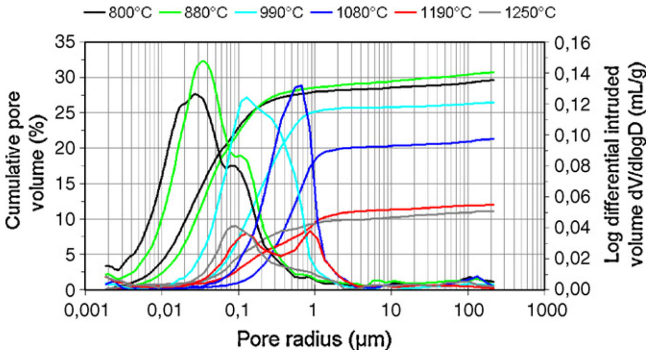

Fig. 4. Pore size distribution and pore volume of clay type A.

simultaneously a pore size distribution high in pores with radii of <0.5–0.85 µm (Figs. 3 and 4). The sintering behaviour is characterised by a wide sintering range (Fig. 1).

Characteristic mineral phases of CT A formed during firing are mullite (Fig. 5) and mullite + cristobalite, respectively, which lead to firm and stable pore boundaries (Fig. 6) and therefore to an increase in strength of the ceramic body.

With increasing firing temperatures the pore size distribution shows an intensive movement of the maximum peak from 0.03 µm at 800 °C towards 0.8 µm at optimal firing temperatures of 1200 °C. Above 1200 °C the maximum peak goes back to pore sizes of about 0.1 µm due to increasing amounts of eutectic melts. At no temperature median pore radii of $R_{50\%} > 1$ µm according to the pore size criteria of BENTRUP[8] for durable microstructures can be achieved. These results apply for all clays of CT A as displayed in (Fig. 3).

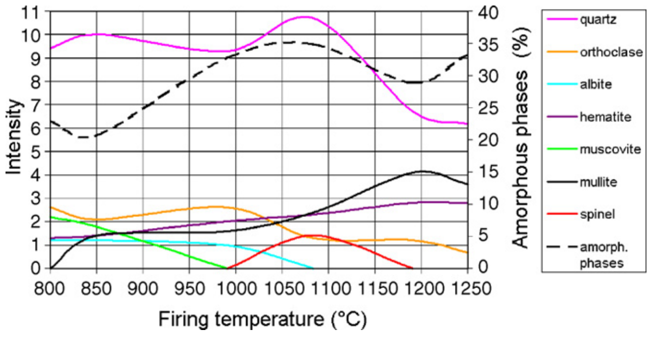

Fig. 5. Development of mineral phases of clay type A against firing temperature.

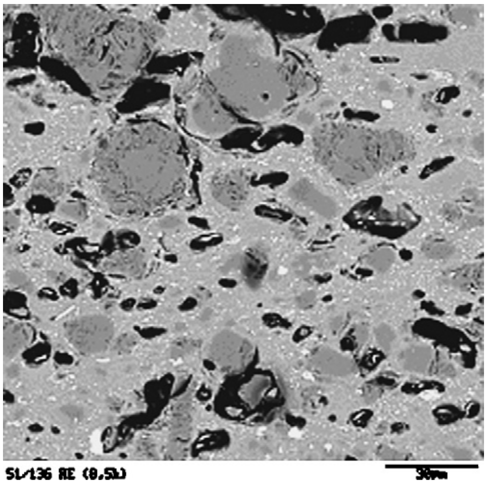

Fig. 6. Microstructure of clay type A formed with the optimal firing temperature of 1250 °C.

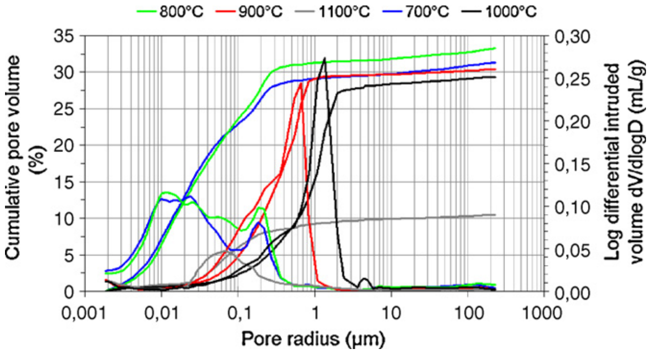

Fig. 7. Pore size distribution and pore volume of clay type B.

The *illitic clay type B* (CT B) is characterised by a rather narrow sintering range (Fig. 1). At optimal firing temperatures of 1050–1100 °C relative dens microstructures with a water absorption of <10–12% occur (Fig. 1).

The pore size distribution of the CT B clays showed, that the maximum amount of pores possesses radii between 0.03 µm and 0.8 µm at 800 °C and 0.63–3.6 µm at 1050 °C.[15] The amorphous phases formed above 1100 °C account for micro pores with radii of 0.1–0.3 µm (Figs. 7 and 10).

The characteristical secondary mineral phases of CT B are spinel and gehlenite which can be transformed into diopside as either a stable or an intermediate phase (Fig. 8).

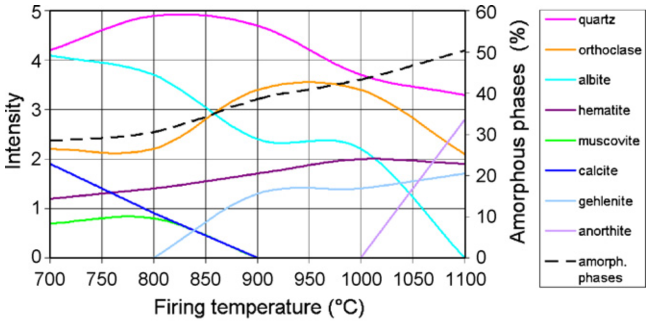

Fig. 8. Development of mineral phases of clay type B against firing temperature.

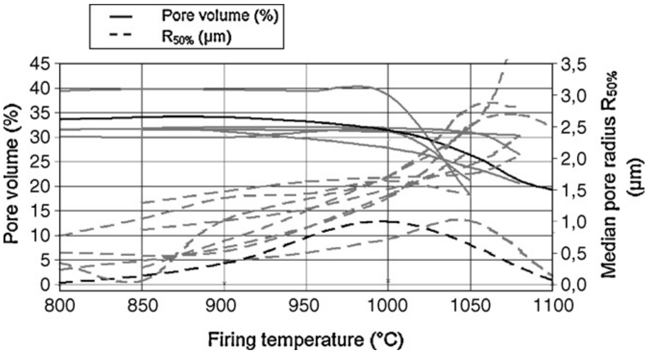

Fig. 9. Development of the pore volume and the median pore radius $R_{50\%}$ of clay type B.

A median pore radius of $R_{50\%} > 1$ µm according to the pore size criteria of Bentrup[8] for durable microstructures cannot be achieved of all of the clays, as can be seen in (Fig. 9).

The *mixed-layer clay type C* (CT C) is also characterised by a relatively narrow sintering range (Fig. 1), which leads to very similar micro-structures from 800 °C to 970 °C and 1000 °C, respectively. The microstructural densification takes place above firing temperatures of 1000 °C and causes a water absorption of 10–15% between temperatures of 1050 °C and 1100 °C. Furthermore, the clays showed a tendency towards bloating due to the constant firing conditions for all clay types (Figs. 11 and 14).

During the sintering process the radii of the maximum amounts of pores develop from 0.07–0.7 µm at 800 °C to 0.65–7.5 µm at 1000–1050 °C (Fig. 11). However, a movement of the maximum peak of the pore size distribution graph back to micro pores due to liquid phase reactions only occur in two clays of that type at a temperature of 1050 °C. To a large extend, median pore radii of $R_{50\%} > 1$ µm according to the pore size criteria of Bentrup[8] can be achieved at higher temperature ranges (Fig. 12).

As stable secondary mineral phases of CT C spinel, gehlenite and anorthite or diopside can be identified (Fig. 13).

The *carbonate-containing clay type D (CT D)* displays an increasing porosity during decarbonation of the carbonates until

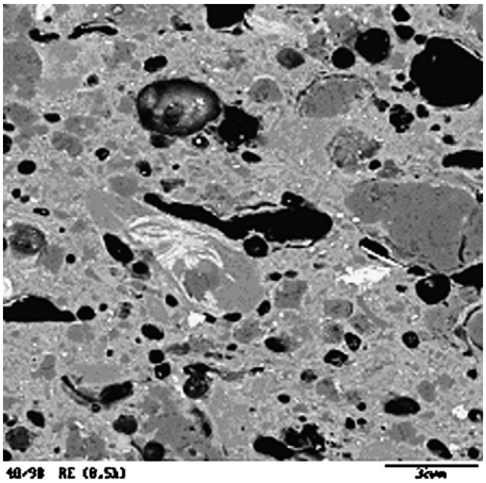

Fig. 10. Microstructure of clay type B formed with the optimal firing temperature of 1100 °C.

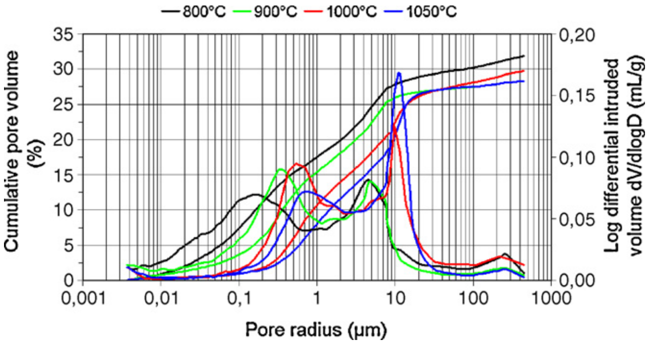

Fig. 11. Pore size distribution and pore volume of clay type C.

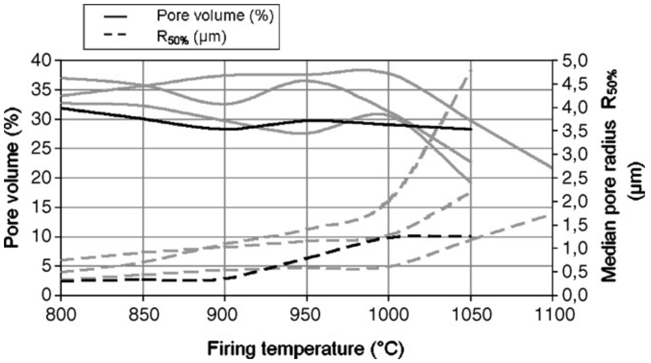

Fig. 12. Development of the pore volume and the median pore radius $R_{50\%}$ of clay type C.

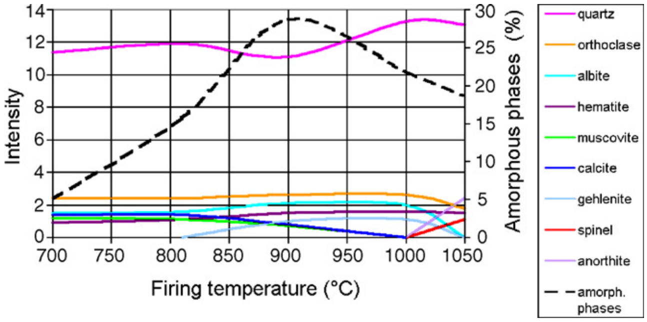

Fig. 13. Development of mineral phases of clay type C against firing temperature.

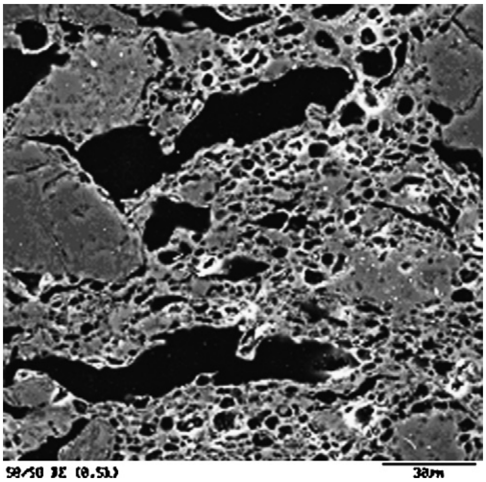

Fig. 14. Microstructure of clay type C formed with the optimal firing temperature of 1050 °C.

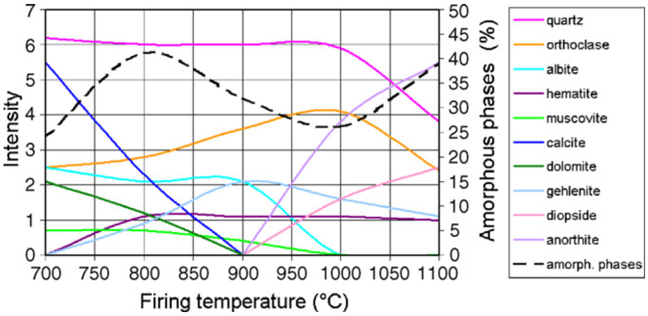

Fig. 15. Development of mineral phases of clay type D against firing temperature.

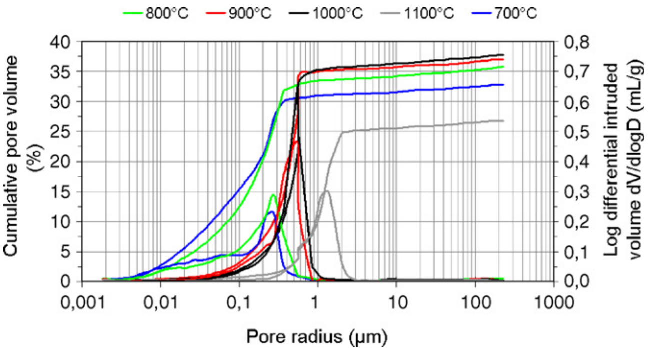

Fig. 16. Pore size distribution and pore volume of clay type D.

approx. 1000 °C. The densification of the microstructure starts between 1000 °C and 1050 °C due to liquid phase reactions and leads to a water absorption of approx. 15%. In addition, there is a relatively narrow sintering range (Fig. 1). The microstructure of CT D formed with the optimal firing temperature of 1100 °C is shown in Fig. 18.

The characteristic secondary mineral phases formed within clays of this clay type are gehlenite, diopside and esseneite (Fig. 15).

During firing there is only a little movement of the pore radii which develop from 0.6–1.0 µm at 800 °C to 0.8–1.2 µm at 1000 °C (Fig. 16). Moreover, in only one clay there is a movement of the pore radius back to about 0.6 µm. Except for three clays median pore radii of $R_{50\%} > 1$ µm according to the pore size criteria of BENTRUP[8] for durable microstructures can be achieved (Fig. 17), which is contradictory to the experiences and applications of those clays in praxis. Clays of CT D are mainly used in thermal insulating bricks, but not as frost resistant ones for applications outside.

3.3. Impact of additives

The influence of the use of industrial wastes in ceramic bodies on their microstructure can be introduced by first results of a current research project and are exemplified by clay type A:

Glass and stone powders utilised in clay type A act as grogging and fluxing agents during the sintering process. The latter leads to an earlier microstructural densification and thus to a movement of the sintering range to lower firing temperatures (Fig. 19).

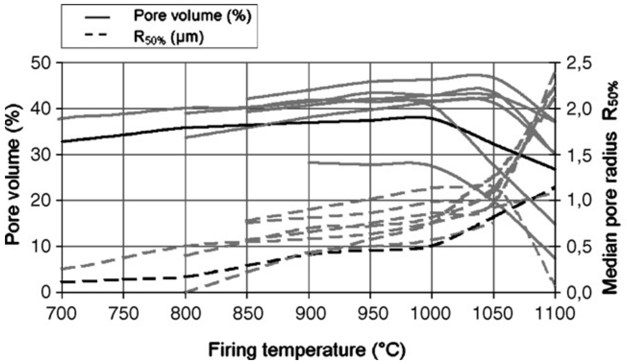

Fig. 17. Development of the pore volume and the median pore radius $R_{50\%}$ of clay type D.

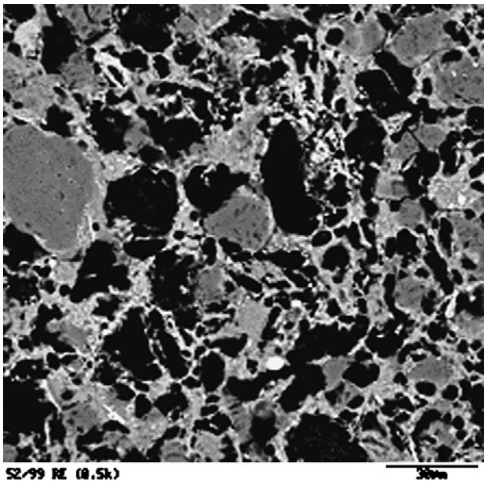

Fig. 18. Microstructure of clay type D formed with the optimal firing temperature of 1100 °C.

By substituting the clay with 25% and 30% of the glass powder wollastonite as a new secondary mineral phase can be analysed, which is responsible for a stabilisation of the pore boundaries and thus account for an increase in strength. Moreover, there is an increasing amount of cristobalite with increasing amounts of glass powder. In contrast, the substitution of clay by 25% and 30% of stone powders leads to the formation of spinel (Fig. 20).

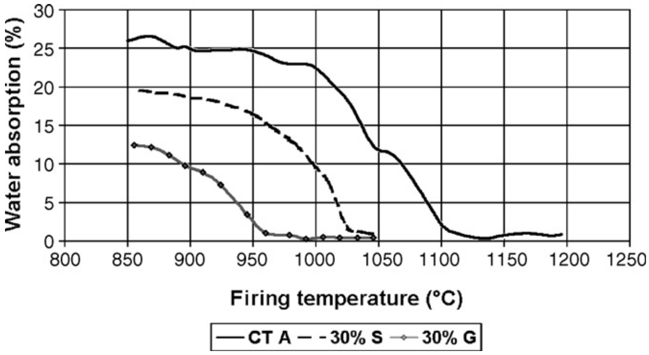

Fig. 19. Influence of glass and stone powders on the development of water absorption of CT A.

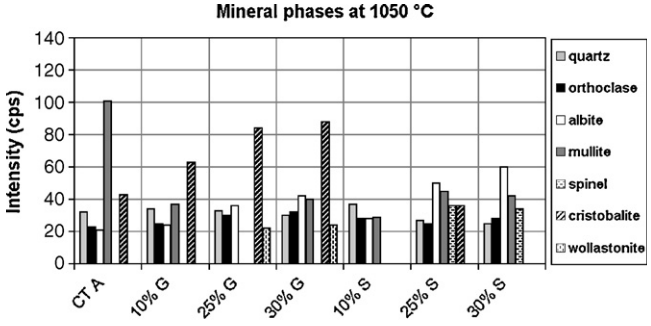

Fig. 20. Influence of glass and stone powders on the development of the mineral phases in clay type A.

The microstructure in Fig. 21 shows that the pore size increases conspicuously due to the use of glass and stone powders in ceramic bodies, which can be proofed by mercury intrusion porosimetry (Fig. 22).

In conclusion, the utilisation of sintering agents can lead to a decrease of the firing temperature between 25 °C and 210 °C compared to the pure clay. The highest energy efficiency can be obtained for clay type A, which means an energy saving of up to 290 kJ/kg fuel.

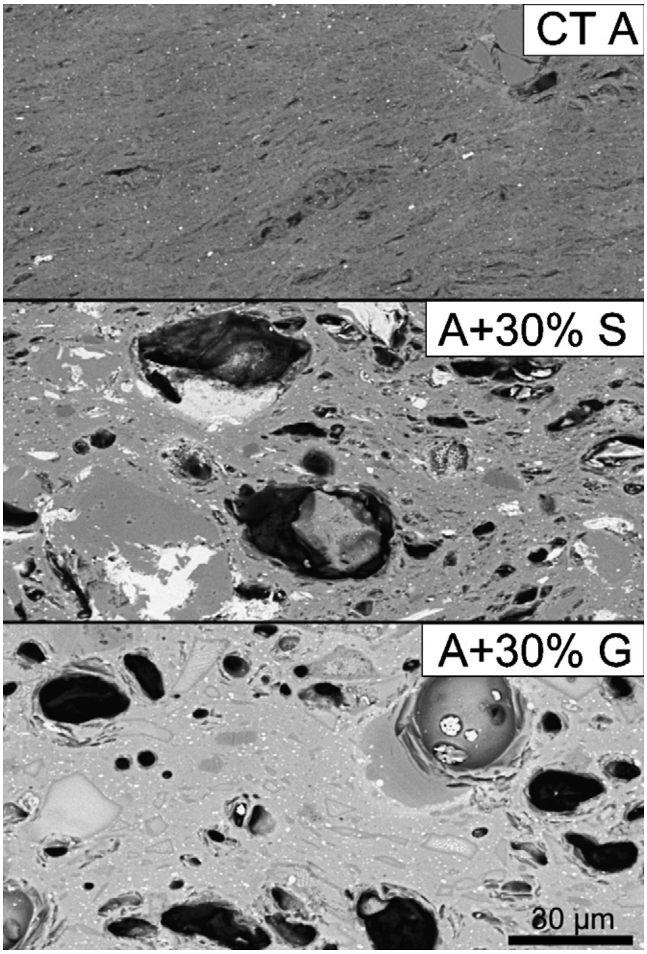

Fig. 21. Influence of glass and stone powder on the microstructure of clay type A at 1050 °C.

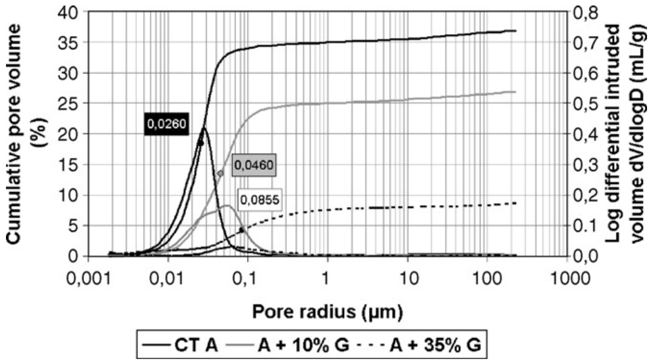

Fig. 22. Influence of glass powder on the development of pore volume, pore size distribution and the median pore radius $R_{50\%}$ of clay type A.

Detailed results concerning the utilisation of additives in bricks with respect to the four clay types will be published in the near future.

4. Conclusions

The comparison of the microstructural development of the four clay types during firing from 800 °C to 1100 °C (CT B, C and D) and to 1250 °C (CT A), respectively, demonstrated that there are significant differences in their sintering behaviour. Each of the clay types shows characteristical secondary mineral phases at varying temperatures which are necessary for the stabilisation of the microstructure. Furthermore, different amounts of capillary-active and sorption-active pores as well as different tendencies of the pore sizes back to micro pores (<0.3–0.5 μm) with increasing amounts of liquid phases had been determined for each clay type. Thus, it will be possible to derive user-oriented predictions for optimised durable microstructures of the final bricks taking into consideration an energy efficient setting of the firing conditions. On closer examination of the obtained results, the indirect conditions for durable microstructures according to BENTRUP[6] and MAAGE[7] cannot be affirmed completely.

For example, the microstructures of the kaolinitic clay type A fully meet the conditions according to MAAGE[7] over all temperature ranges, but do not conform at any temperature to the condition of BENTRUP[6] ($R_{50\%} > 1$ μm). On the other hand, the carbonate-containing clay type D corresponds to both named conditions, which is contradictory to the praxis. Usually, the latter clays are used for thermal insulating and porous bricks. In contrast, the bases of frost resistant clinker bricks are kaolinitic clays. The modification of the pore radius limits with respect to the clay type as well as their extension towards mineral phase aspects can be made as follows:[15]

- Modifying the median pore radius condition for kaolinitic clays from $R_{50\%} > 1$ μm to $R_{50\%} < 0.8$ μm.
- Limiting the amounts of micro pores ($R < 0.5$ μm) to <25–30%.
- Assessing the amounts of those secondary mineral phases that, with respect to the clay type, lead to high amounts of pore sizes between 1 and 5 μm and that form elastic pore bound-

aries from stable and mainly crystalline phases. In contrast, liquid phases account for brittle and inelastic microstructures, which in addition can be associated with so called ink bottle pores.

Acknowledgement

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