THE ISOLATION OF WOLLASTONITE CRYSTALS IN CLAY CERAMIC BODIES

M. Adlung-Baykara

evo - Silicatforschung
Research Institute Prof. Dr. Dr. Stegmüller
Benzstr. 18, 89079 Ulm, Germany

1. AIM OF THE WORK

In the field of building ceramics as well as for the testing of materials containing chalk the system SiO_2-Al_2O_3-CaO is very important for practice. Especially the part $CaO.SiO_2$-$CaO.Al_2O_3.SiO_2$-SiO_2 (Wollastonite - Anorthite - Silica) of the system has a high technical importance for the production of wall and floor tiles. Although many publications are available there are many open questions which have to be looked at under consideration of new technological points of view.

Using natural wollastonite is advantageous for the rapid firing of clay ceramic mixtures and also with regard to glazing and enamel if we do not consider the costs which are very high.

The production of synthetic wollastonite should lead to a reduction in costs. However, the different possibilities to produce synthetic wollastonite require a special technology because its use is also very expensive due to the present energy situation and the increasing production costs.

First it was therefore necessary to study the solid-state reaction between CaO and SiO_2 during the synthesis of wollastonite and to test which cations, in exchange for Ca^{2+}, have an activating and which cations have a passivating effect on the formation of wollastonite. It would also become interesting to use less pure basic raw materials if they were selected well-aimed with regard to their impurities.

Moreover it was also dealt with the question of stability of the modification of calcium monosilicate α/β - wollastonite.

In all clay ceramic mixtures the wollastonite is decomposed totally or partly in favour of the formation of anorthite. It could be shown how to stabilise the imbalance wollastonite / clay substances by means of technology. α- or β- wollastonite crystals could be isolated in the ceramic matrix depending on the product.

2. FORMATION OF WOLLASTONITE IN CLAY CERAMIC MIXTURES

2.1 CHEMICAL COMPOSITION OF THE MODEL RECIPE

The chemical composition of the model recipe in the equilibrium system was reduced to three substances:

54 M.-% SiO_2
21 M.-% Al_2O_3
25 M.-% CaO

2.2 TESTING OF WALL TILE MIXTURES

The model recipe listed in the equilibrium system CaO - Al_2O_3 - SiO_2 consists of the clay - kaolin mixture and the matters reacting to wollastonite.

The formation of wollastonite during firing has an advantageous influence on the firing behaviour. Sudden extension anamalies as e. g. the α - β quartz conversion depend on the preparation of the body.

2.3 THE PRESSING METHOD HAS AN INFLUENCE ON THE FORMATION OF STRUCTURES

Wall tiles are usually produced by compacting spray - dried granular bodies. But this procedure is very energy consuming. There have been attempts to replace this procedure by dry-milled granular bodies.

The pellets produced from calcit and quartz sized 1 mm Ø were coated with amorphous silica. In the last step clay material was added and at a stage of 6 % moisture they were pressed to wall tiles. These samples were marked by "P" (figure 1, 2 and 3).

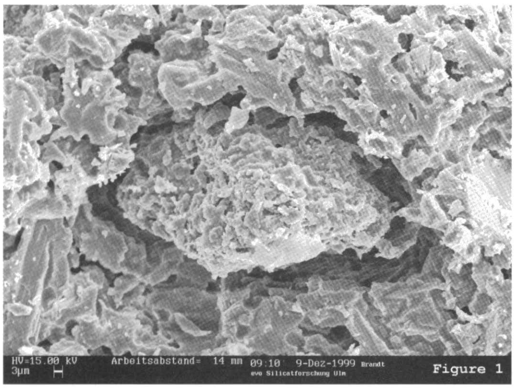

Figure 1. *SEM photograph from pellets after firing.*

Figure 2. *SEM photgraph from body of wall tile*

The samples marked by "H" were produced by homogenising a mixture of calcit, clay and quartz. These samples were pressed to wall tiles at a stage of 6 % moisture.

The dilatometer curve of sample "P" is linear, the expansion/shrinkage-curve (ES) of sample "H" and clay bonding "B", however, show an anomaly in the region of quartz conversion, which is disadvantageous for the fast firing (figure 4).

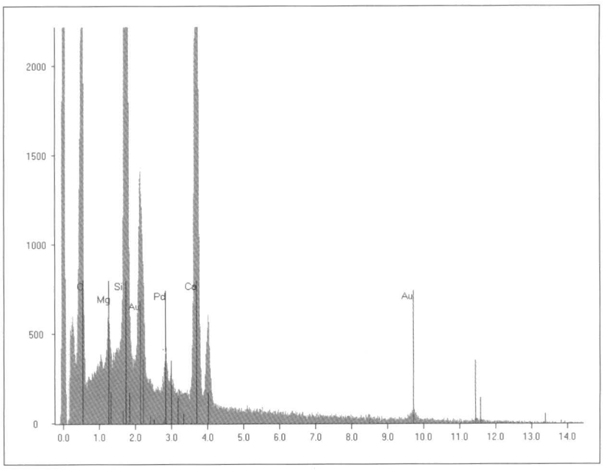

Figure 3.*EDX from pellets containing more wollastonite.*

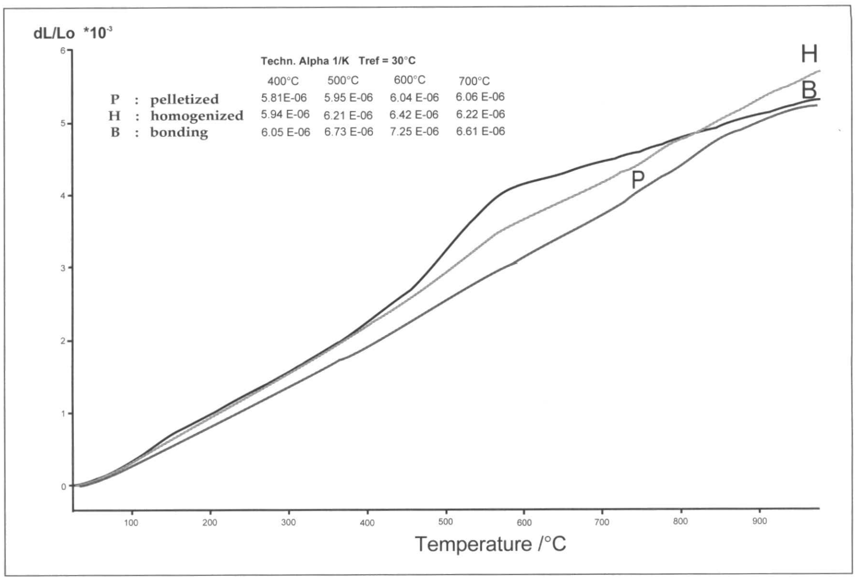

Figure 4. *Dilatometer curve from samples "P", "H" and "B".*

With regard to the technical characterisitcs there is no difference between the wall tile mixture "P" of the model recipe and the mixture "H". But there are different values in connection with the flectional strength. The mixture "H" shows values of about 15, 23 N/mm^2 and it is exceeded by the mixture "P" with a value of 19,45 Nmm^2.

The technical data of the material "P" are listed below:

	Mineral content in weight		
Phase	B	P	H
Anorthite	54.6	67.6	58.5
Wollastonite		26.7	26.4
Quartz	45.4	5.7	15.0

Table 1.A quantitative phase analysis from sample "P."

Firing programme:

Heating -up-Speed (°K/h):	400
Firing temperature (°C):	1.100
Holding time (h):	0,5

	x	s	confidence interval
Flectional strength (N/mm^2)	29,93	5,69	$35,89 < \mu \leq 23,97$
Water absorption (%)	17,68	3,09	$20,93 < \mu \leq 14,44$
Raw density of the fired mixture (g/cm^3)	2,07	0,10	$2,17 < \mu \leq 1,96$

***Table 2.** Technical data of the material.*

$CTE_{20\text{-}600^{\circ}}$ $6{,}76.10^{-6}K^{-1}$

3. THE ISOLATION OF WOLLASTONITE CRYSTALS

The experiments show that wollastonite crystals might be formated as a result of the pelletizing process during the firing. The temperature stability of wollastonite depends on the different kind of mineralizers incorporated in the wollastonite lattice.

The following can be recorded after X-ray analysis, on the basis of the activating and passivating formation of wollastonite, the only newly developed phases, the quantity of melting phase and the decomposition of quartz:

1. In the coordinating system with the coordinates cation radius and electronegativity (according to Pauling) we get two separate groups: one between the limits 0,7 and 1,3 and the other between the limits 1,3 - 2,0. With increasing temperatures (900 - 1.200° C) the number of cations having an activating effect on the formation of wollastonite is increasing within the grouping 0,7 and 1,3 and are decreasing in the groupings 1,3 to 2,0.
2. The conversion temperature of quartz - cristobalite is shifted to 1.100° C in the case of 5 Mol-% V^{5+} and in the case of 2 Mol-% K^+, Rb^+, $Sn2^+$ and CaF_2. At the same time a relative decrease of β- $CaSiO_3$ - quantity could be recognized.
3. The conversion temperature from β- to α - $CaSiO_3$ increases in the case of an addition of 2 Mol-% Mg^{2+} (MgO, MgF_2), Mn^{2+}, Cr^{3+} and Mo^{6+} as well as of 5 Mol-% Cs^+, Mg^{2+} (MgO, MgF_2), Mo^{6+}, W^{6+}, Mn^{2+} and Sn^{2+}.
4. The formation of wollastonite not only depends on the cations but also to a high degree on the anions. The kations introduced as fluorides have a better mineralizing effect than the oxides.

4. INFLUENCE OF OXIDES ON AT TEMPERATURES BETWEN 1.000 AND 1.200° C

The influence of different oxides on the sintering of α/β-wollastonite at three temperatures was carefully examined. All additives showing a positive effect are in a certain area of the coordinate system (cation radius - electronegativity difference). This area is marked off with a dotted line.

The oxides, the M-O bond of which has an electronegativity difference of less than 2.0, show their activating effect between 900 and 1.000 ° C. The alkaline and alkaline-earth oxides with a high ionic bond portion of more than 63 % (electronegativity difference of 2.3) cause a mineralization between a temperature of 1.000 and 1.200 ° C.

Only at a temperature of 1.100 ° C the groupings are balanced and have an activating effect on the sintering of wollastonite.

5. THE INFLUENCE OF THE LIQUID PHASE ON THE SINTERING PROCESS

Another possibility to support the formation of silicates is to use liquid products.

The formation of alkaline - earth silicate can be accelerated by keeping the crystallizing alkaline - earth silicates in a certain balance with a liquid phase, that means that the synthesis is led very close to the melting point of the pure alkaline - earth silicates.

A liquid phase on the grain interface increases the diffusion of the grain interface. The formation of calciummonosilicates can be accelerated if the chemical composition of the liquid is similar to the one of the crystallizing alkaline - earth silicates. An addition of phosphor - slag or glassy recycling products containing CaO supports the mineralizing effect.