Phase reactions in the brick firing process of V-doped clay

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Abstract: The phase reactions of V-doped clays in brick burning processes are studied to evaluate the utilization of V-containing wastes in brickworks. V$_2$O$_5$ was admixed to clay and annealed at temperatures between 200 and 1000 °C. The formation of mullite, cristobalite, and a pseudobrookite compound is observed between 700 and 800 °C. These phases do not occur in pure clay annealed in the corresponding temperature range. The samples were investigated with X-ray powder diffraction methods, quantitative analyses were performed with the Rietveld method and chemical analyses with X-ray fluorescence spectroscopy. Analytical Transmission Electron Microscopy showed incorporation of vanadium and iron in mullite.

Key-words: brick burning, heavy metal contaminated waste, vanadium, cristobalite, mullite, X-ray powder diffraction (XRD), Rietveld analysis, Analytical Transmission Electron Microscopy (ATEM).

Introduction

Deposition of heavy metal contaminated wastes (e.g. sewage sludge, waste incinerator ashes etc.) could be avoided by immobilization of the heavy metals as constituents in mineral phases. The immobilization can be achieved by thermal treatment as described by Förstner (1995) and discussed by Margane (1992). A possible procedure would be the utilization of clay-waste mixtures in brick burning processes typically at temperatures around 1000 °C. Meanwhile, the process of manufacturing bricks doped with heavy metals is already established, e.g. at Grehl brickworks in Humlangen, southern Germany. However, the formation of phases and the details of heavy metal incorporation are not known. Some indication of the brick’s solubility behavior is achieved by leaching tests according to DEV S4 DIN 38414 (1984). But these tests do not explain the long term properties of the material, especially under non standard conditions in acidic or basic environments. Dondi et al. (1997) describe the mobilization of vanadates and chromates during firing processes. The vanadates migrate to the surface of ceramic materials in the presence of water resulting in efflorescences which affect the long term properties of the ceramic product. The solubility of vanadium increases with increasing annealing temperature.

A comprehensive crystal chemical description of the phase formations and reactions during brick burning in the presence of heavy metals is needed for an extensive and more reliable interpretation of the complex processes. It is compared with the corresponding processes during annealing of natural clay without additives. Salmang & Scholze (1983) describe the processes of brick burning using pure clays consisting of clay minerals, feldspar and quartz. At temperatures between 500 and 700 °C the dehydroxylation of the clay minerals, especially kaolinite, is observed (Bellotto et al., 1995). Kaolinite transforms to metakaolinite. Last traces of -OH groups are removed and the sheet structure collapses between 800 and 950 °C. Cristobalite and mullite are formed upon further heating between 1100 and 1400 °C (Brindley & Nakahira, 1959; Gualtieri et al., 1995), according to the transformation:

$$3 \text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \rightarrow 3 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4 \text{SiO}_2 + 6 \text{H}_2\text{O}.$$
The formation of cristobalite upon addition of V₂O₅ is described by Bruhns & Fischer (2000). In the system SiO₂-V₂O₅-M₂CO₃ (M = Na, K), the crystallization of a cristobalite like phase starts at about 800 °C. With increasing amounts of vanadium, the formation of alkali vanadates is observed. Phase diagrams of the systems SiO₂-V₂O₅ indicate partial melting at temperatures above 661 °C and for Al₂O₃-V₂O₅ above 658 °C (Gravette et al., 1966; Barham, 1965). In the presence of a liquid phase, a higher reactivity of the system is expected and formation of cristobalite occurs in lower temperature regions.

Decomposition of illite starts at about 850 °C but traces of illite are still observed up to 1000 °C (Kromer & Schüller, 1974). Depending on the chemical composition of illite, a wide variety of resulting phases is possible in clay systems, e.g. hematite, corundum, feldspar, leucite, spinel etc. (Jasmund & Lagaly, 1993). Mazzucato et al. (1999) describe the high temperature dehydroxylation of muscovite which is the K-rich mica structurally closely related to illite. A dehydroxylated phase is observed between 700 and 1000 °C transforming to mullite at higher temperatures. In brick burning processes, illite acts as a flux (Salmang & Scholze, 1983). The presence of liquid phase is important for further reactions and influences properties and quality of the burned brick. Quartz is expected to participate only in the reactions at temperatures above 1000 °C.

The aim of this work is to determine the influence of vanadium on the phase reactions in brick burning processes of V-doped clay.

**Experimental**

**(1) Sample treatment and calcination**

The raw clay material used for the syntheses was provided by Ziegelwerk Grehl, Humlangen, Germany. It consists of quartz, kaolinite, illite, minor amounts of rutile and hematite, and about 17 wt.-% of amorphous phases (Fig. 1) as determined by Rietveld analyses using an internal standard.

It was homogenized in an agate mortar and pressed to pellets of 13 mm diameter for the annealing experiments. Kaolinite is very sensitive to mechanical treatment. A destruction of the crystal structure could be caused by grinding or pressing. Kristóf et al. (1993) showed the influence of the amorphization of kaolinite on its thermal behavior and the formation of mullite. In this work great care was bestowed to avoid these effects as far as possible. Hand grinding up to 15 min. did not show any
significant effect in powder diffraction patterns of either the raw or the annealed material.

In addition to the pure clay samples, further batches were mixed with 1, 2, and 5 wt.-% V$_2$O$_5$ and treated similarly. The experiments with addition of 5 wt.-% V$_2$O$_5$ showed the most evident mineralization effects so they are compared in the following with the pure clay samples.

For the thermal treatment of samples containing volatile vanadium compounds, special care was taken to avoid contamination of the furnace environment. Since corundum tubes and crucibles are permeable to vanadium, they are not suitable as containers for the calcination experiments. A silica glass tube (Fig. 2) was used to protect the furnace from contamination. The tapering ends of the synthesis pipe allow a definite gas flow and the adjustment of different reaction atmospheres. The following syntheses were performed under oxidizing conditions with air. The samples were prepared in silica glass boats. All samples were annealed in the range between 200 and 1000 °C for 17 h with a heating rate of 200 °C/h. In the temperature range around 500 °C (decomposition of kaolinite) syntheses were performed in steps of 50 °C. Additionally, the specimens containing vanadium were annealed in steps of 50 °C up to 800 °C to describe the reaction sequence.

(2) X-ray fluorescence spectroscopy (XRF)

Chemical analyses were performed using a Philips 1404 X-ray fluorescence spectrometer at the Institute of Mineralogy, University of Mainz. The XRF analysis of the pure clay yielded weight fractions of 67.48 % SiO$_2$, 18.84 % Al$_2$O$_3$, 3.17 % Fe$_2$O$_3$, 1.37 % TiO$_2$, 0.16 % CaO, 0.4 % MgO, 0.15 % Na$_2$O, 1.72 % K$_2$O, and 0.03 % P$_2$O$_5$. The deviation to 100% was determined as weight loss due to dehydration and water desorption.

(3) X-ray powder diffraction (XRD)

XRD patterns were recorded using a Philips PW 1050 powder diffractometer with secondary monochromator and a Philips PW 3050 powder diffractometer with primary monochromator. Data were collected using CuK$_{α1}$ radiation at room temperature in the range between 5 and 120° 2θ and steps of 0.02° 2θ. All refinements were performed with the Philips PC-Rietveld plus program package (Fischer et al., 1993), background values were set by hand. Quantitative analyses were performed using the scale factors from the Rietveld refinements. Amorphous fractions were determined with ZnO as internal standard. The following structure models were used for the simulation of the powder patterns: quartz by Will et al. (1988), cristobalite by Pluth et al. (1985), kaolinite by Bish & von Dreele (1989), mullite by Ban & Okada (1992), hematite by Blake et al. (1966), rutile by Abrahams & Bernstein (1971), ZnO by Kisi & Elcombe (1989), V$_2$O$_5$ by Ketelaar (1936), pseudobrookite by Hamelin (1958). Input parameters for the simulation of the illite structure were taken from muscovite data determined by Richardson & Richardson (1982) which showed the best fit with the illite among all available data on muscovites. Zöller (1994) demonstrated that the structural parameters of muscovite, adapted to the illite cation distribution and optimized by distance least squares refinements, closely resembles the illite structure as analysed by electron diffraction.

Reliable structural data do not exist for illite due to its bad crystallinity and variable chemical composition in natural clay. Using data for illite based on the muscovite model recently published by Gualtieri (2000) did not improve the refinements in this work.

(4) Analytical Transmission Electron Microscopy (ATEM)

Analytical Transmission Electron Microscopy was performed at the Deutsches Zentrum für Luft- und Raumfahrt (DLR) in Köln using a Philips EM 430 analytical microscope (300 kV accelerating volt-
Further studies of thin sections using a petrographic microscope failed as well as additional analyses with an electron beam microprobe. The crystallites formed in the annealing process were too small and could not be resolved by these microscopic methods.

Results

The XRD pattern of the raw clay material (Fig. 1) shows a composition of quartz, rutile, hematite, kaolinite, and illite. Illite was identified as 2\(M_1\) polytype by its characteristic reflections at 25.3 and 27.9° 2\(\theta\) which match the (114) and (114) peaks of the 2\(M_1\) modification (Moore & Reynolds, 1989). Weight fractions of the crystalline phases and the amorphous compound are plotted in Fig. 1. Quantification is a crucial point in multi phase analyses, especially when clay minerals are present. Possible sources of errors in quantitative Rietveld analyses are anisotropic peak broadening caused by disordered structures, incorrectly determined chemical compositions, and insufficient crystal structure models. It is expected that the effect is most pronounced for illite and kaolinite which undergo continuous changes in the annealing process. In order to get a rough estimate of the errors, the chemical composition of muscovite, used to simulate the powder diffraction pattern of illite, has been varied between typical illite and muscovite compositions. The resulting weight fractions differed by less than 2 wt.-%, which indicates that the quantitative analyses are not much affected by using muscovite data for the simulation in lack of reliable structure models of illite. The phase formations in the pure clay material between 200 and 1000 °C are shown in Figure 4 and the corresponding weight fractions of the single phases are plotted in Figure 1. Samples of clay mixed with V\(_2\)O\(_5\) (5 wt.-%) and heated in the range 200 to 1000 °C show different phase compositions (Fig. 5). Weight fractions of the crystalline phases and amorphous compounds as derived from the Rietveld analyses are given in Figure 6. XRF analyses proved that there is no loss of vanadium content during burning processes.

The reaction sequence up to about 700 °C is similar in pure clay and in vanadium containing samples: kaolinite decomposes and then disappears above 650 °C. Syntheses performed at higher temperatures reveal remarkable differences. While the mineral content in the pure clay samples remains qualitatively and quantitatively more or less stable except the decomposition of kaolinite, it changes significantly in the V-doped samples. First traces of mullite are detected at 750 °C with increasing content towards higher annealing temperatures. At 1000 °C, an amount of about 26 wt.-% is deter-
Fig. 4. Observed (crosses) and calculated (lines) powder diffraction patterns from Rietveld refinements of pure clay annealed between 200 and 1000 °C. Q: quartz, Z: ZnO, H: hematite, R: rutile, I: illite, K: kaolinite.

20 nm crystals of mullite with Analytical Transmission Electron Microscopy (ATEM) yielded an amount of 3.2 mole-% vanadium and 3.8 mole-% iron in mullite of the sample synthesized at 1000 °C which explains the observed deviations. Further cell parameters of vanadium and iron doped mullite described by Schneider & Rager (1986) and Schneider (1990) (Table 1) are plotted in Figure 7. The $b$ and $c$ lattice constants, especially of the iron doped samples, correlate with the shaded zones. The syntheses temperatures are significantly higher (> 1300 °C) than the temperature range used in our study. We observe an expansion of the cell parameters of mullite already at 800 °C. Obviously, the addition of vanadium oxide promotes the formation of mullite in a clay system. Transformation of kaolinite to metakaolinite yields the precursor and vanadium is incorporated in the structure.

The refined lattice constants of this mullite phase, derived by Rietveld refinement, show remarkable deviations from the starting parameters given by Ban & Okada (1992) (Table 1). Fischer et al. (1996) plotted several mullite lattice constants and showed the relationship between the cell parameters and the molar content of Al$_2$O$_3$. These curves are plotted in Figure 7. The shaded areas indicate the range of lattice constants determined from the four mullites from our studies annealed at different temperatures (Table 1). Usually, the chemical composition of mullite is determined by its $a$ cell constant which is linearly related to the molar Al$_2$O$_3$ content of mullite. The lattice constants determined here clearly deviate from this relationship since the $b$ and $c$ parameters do not match with the curves at the positions of any of the observed $a$ constants. Further investigations of 50 x
Furtheron, the crystallization of α-cristobalite starts at 800 °C as well. Just as mullite, cristobalite is not formed in the pure clay samples in the temperature range up to 1000 °C. The reaction influenced by vanadium was determined by Bruhns & Fischer (2000): we observed cristobalite formation in the system SiO₂-V₂O₅-M₂CO₃ (M = Na, K) in the same temperature range. The reduction of the complex clay system to a composition of only three components allowed the syntheses and detailed determination of cristobalite. Experiments with XRD, IR, DTA, and MAS NMR were performed. We did not find any indication for V-incorporation in the cristobalite structure. Clay syntheses containing vanadium yield an additional mineral phase which is not detected in pure clays. At 800 °C, a pseudobrookite compound (Fe₂TiO₅) crystallizes. Its content increases with increasing annealing temperature while rutile and hematite decrease simultaneously. Above 900 °C, neither rutile nor hematite are detected in X-ray patterns. Formation of pseudobrookite influenced by V₂O₅ was simulated in a system containing TiO₂, Fe₂O₃, and V₂O₅. The oxides were admixed according to the stoichiometric composition of pseudobrookite. These batches were annealed under the same conditions (1000 °C, oxidic atmosphere) as the clay samples. The amount of Fe₂TiO₅ increases significantly with the addition of vanadium. Additionally, an iron-vanadate compound (FeVO₄) occurs which incorporates vanadium. The powder patterns of this pseudobrookite did not provide any indication for a chemically modified phase. However, it cannot be ruled out that some V has entered the structure which does not show in the X-ray pattern. Chemical analysis was not possible due to the extremely small crystals.

As mentioned above, syntheses in pure clay sys-
tems did not show any formation of new mineral phases in the temperature range between 800 and 1000 °C. After decomposition of kaolinite, an increase in the amorphous amount up to about 45 wt.-% at 1000 °C is observed (Fig. 1). The contents of rutile and hematite are approximately constant.

In pure clay samples, illite is not completely decomposed during heating. It is detected up to 1000 °C, although in very poor crystallinity. The beginning destruction of the structure is evident in the Rietveld refinement. At temperatures above 600 °C a peak broadening is observed and the intensities decrease. Only the intensity of the peak at 19.7° 2θ remains more or less constant. While transformation processes and high-temperature phases are described for muscovites, a corresponding model for illite is not available so far. The formation of a second high-temperature phase, similar
Table 1. Lattice constants of pure and transition metal-doped mullites.

<table>
<thead>
<tr>
<th></th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ban &amp; Okada (1992)</td>
<td>Pure mullite (3:2)</td>
<td>7.5459(2)</td>
<td>7.6937(2)</td>
</tr>
<tr>
<td>Schneider (1990)</td>
<td>Mullite (8.7 wt.-% V₂O₅)</td>
<td>7.555(2)</td>
<td>7.711(3)</td>
</tr>
<tr>
<td></td>
<td>Mullite (10.3 wt.-% Fe₂O₃)</td>
<td>7.574(1)</td>
<td>7.726(1)</td>
</tr>
<tr>
<td>Schneider &amp; Rager (1986)</td>
<td>Mullite (3.64 wt.-% Fe₂O₃)</td>
<td>7.5507(5)</td>
<td>7.7000(6)</td>
</tr>
<tr>
<td></td>
<td>Mullite (11.1 wt.-% Fe₂O₃)</td>
<td>7.571(1)</td>
<td>7.725(1)</td>
</tr>
<tr>
<td>This study</td>
<td>800 °C</td>
<td>7.604(2)</td>
<td>7.741(2)</td>
</tr>
<tr>
<td></td>
<td>900 °C</td>
<td>7.5953(6)</td>
<td>7.7037(6)</td>
</tr>
<tr>
<td></td>
<td>950 °C</td>
<td>7.589(1)</td>
<td>7.723(1)</td>
</tr>
<tr>
<td></td>
<td>1000 °C</td>
<td>7.582(1)</td>
<td>7.723(1)</td>
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The reaction sequence shows the evident influence of addition of vanadium on the phase formation in clay systems. Several compounds as illite, hematite, and rutile decompose or react to form new phases not observed in the pure clay systems. The formation of mullite and cristobalite is observed in a temperature range much below their expected fields of stability. With the increasing amount of mullite and cristobalite the amorphous content, mainly metakaolinite, decreases. V₂O₅ supports the reaction and some of the vanadium together with iron from Fe₂O₃ participates in the crystallization of mullite.

We assume that vanadium is not incorporated, or only in very small traces, into the structure of cristobalite as discussed by Bruhns & Fischer (2000). Similar reasoning applies to pseudobrookite which crystallizes in the presence of vanadium without a distinct indication of V-incorporation. The vanadium, added as V₂O₅ to the sample, is not completely exhausted by the V-mullite which incorporates only a small fraction of the initial amount of vanadium. The remaining quantity cannot be assigned to an identified mineral phase. We assume that additional vanadate compounds crystallize as well, in quantities below the detection limits of our analytical methods. Former investigations (Bruhns & Fischer, 2000) showed the formation of alkali-vanadates during cristobalite syntheses in the presence of vanadium and alkali metals. The syntheses of pseudobrookite, separately performed in this work, yielded an iron-vanadate phase.

These results show that the concept of cation immobilization in the brick burning process is very limited for V-containing materials. It is assumed that only part of the vanadium is bound in silicates (here: mullite) and the rest is expected to form vanadates mainly with alkalis and iron. Since some of these vanadates are soluble in water, its utilization in building materials should be carefully evaluated.

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Conclusion
References


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