

## Novel flux-calcination process of Kieselguhr avoiding formation of crystalline material

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Industrial modification (calcination) of natural Kieselguhr is an advantageous process for better tuning of particle parameters (i.e. enhanced porosity, improved filtration behaviour, etc.). The modification has another beneficial effect by reducing the Cristobalite formation, which is undesired side product of this modification procedure. This paper elucidates the correlation between the art of Kieselguhr calcination and the surface properties with respect to Cristobalite formation. Reaction conditions have been identified, where Cristobalite is selectively formed. This knowledge enables to minimise (or even to avoid) its formation by choosing advantageous processing conditions even at industrial scale. Initially, the micro-scale experiments have been carried out to understand the circumstances on the Kieselguhr surface, where the Cristobalite is formed. Afterwards, these investigations have been further scaled up to the lab and mid-scale production unit.

### 1. Introduction

Kieselguhr (diatomite) is a form of silica composed of the siliceous shells of unicellular aquatic plants. One of the main applications of Kieselguhr is its use as filtering material to clarify liquids in food industry, e.g. beer.

It is generally very fine material and hence not suitable for its direct application in special filtering operations. However, after suitable modification of its particle size (and internal structure) it can be used for example as enhanced filtration agent in brewing industry. The reason therefore is the necessity of different particle's shape and permeability for deep-bed beer filtration (Antoni et al., 2005). The particle agglomeration occurs during calcination. Unfortunately, the calcination process initiates in many cases formation of Cristobalite (one of the three crystalline modifications of silica), which is classified as a carcinogenic component (by International Agency for Research on Cancer). In view of this, the formation of Cristobalite has to be avoided. Thus, if Cristobalite is formed during the calcination of Kieselguhr, it has a negative influence to the overall brewing process.

In general, the spent Kieselguhr from breweries is disposed, and hence there is no recycling for further brewing applications yet. The disposals, containing Kieselguhrs, are frequently used as fertilisers. If the Kieselguhr contains undesired Cristobalite, this application will probably not be possible in next future any more. In this case, a large amount of carcinogenic material containing Kieselguhr has to be disposed on special magazines for hazardous chemicals as reported recently (Schleicher et al., 2008).

Thus, it is of peculiar importance to develop other preparation routes that lead to modified Kieselguhr, without the presence of such crystalline materials. Flux calcination with selected flux agent is one good example to avoid the formation of Cristobalite.

The aim of this contribution is to prepare an industrially applicable modification of pure Kieselguhr by mean of calcination with different flux components, resulting in a very low Cristobalite concentration, that do not affect the environment.

## 2. Experimental

Pure Kieselguhr FN1 obtained from Eagle Pitcher Industries Inc. (E. Begerow GmbH & Co, GmbH, Langenlonsheim, Germany) was calcined in presence and absence of flux components in tubular oven from 25 to 1200 °C with a rate of 10 K/min in a nitrogen atmosphere. The flux component was added as dry powder in a concentration, corresponding to 3 mol. % of the total Kieselguhr amount. The flux component was grinded together with Kieselguhr particles in globe mill for 2 hours. Than the powder was sieved to desired particle size. The benefit of this preparation method is very easy handling of all possible flux components in an industry-like processing. The calcined samples were characterised by X-Ray Diffraction (XRD) analysis and transmission electron microscope (TEM).

### 2.1 XRD Analysis

The XRD data were collected with transmission diffractometer STADI P (STOE Darmstadt) under following conditions:  $\text{CuK}_\alpha$ -radiation ( $\lambda = 1.5406 \text{ \AA}$ ), 40 kV voltage, 40 mA power, measurement pool from 5 up to 60 °2 $\theta$ .

### 2.2 TEM Analysis

Samples for transmission electron microscopy (TEM) were prepared by depositing the sample on a carbon coated copper grid. TEM analysis was performed using a CM-20 STwin transmission electron microscope (Philips/FEY, Holland) at 200 kV.

## 3. Results and discussion

The amount of formation of Cristobalite is found to be dependent the calcination temperature, temperature ramp and duration of calcination. All these parameters have been tested both in micro-scale as well as in a laboratory rotating oven with an aim to learn more about the suppression of Cristobalite formation. The intention is also to propose real processing conditions for industry-scale verification runs. In particular, the purpose of the experiments was to gain deeper understanding on surface processes,

directly influencing the formation of Cristobalite during calcination with the addition of flux-agent.

From the wide pool of possible flux-components alkali-metals in carbonate form were chosen. Especially,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  seem to be the promising representatives (Antoni et al., 2005). Calcined Kieselguhr with addition of different alkali-metal carbonates as a flux-agent (alkali-metal cation interaction with surface of Kieselguhr particle) was analysed by XRD. It is visible that growing cation radius reduces the formation of Cristobalite, see Figure 1. According to Figure 1, the flux-agent applicability for Cristobalite-free Kieselguhr decreases in the order:  $\text{Cs}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3$ . In the case of cesium carbonate, the loading of the surface with Cristobalite is lower than by calcination without flux-agent addition. Details about the cation radius impact on the surface modification during flux-supported calcination of FN1 Kieselguhr are given very recently (Smejkal et al., 2009).

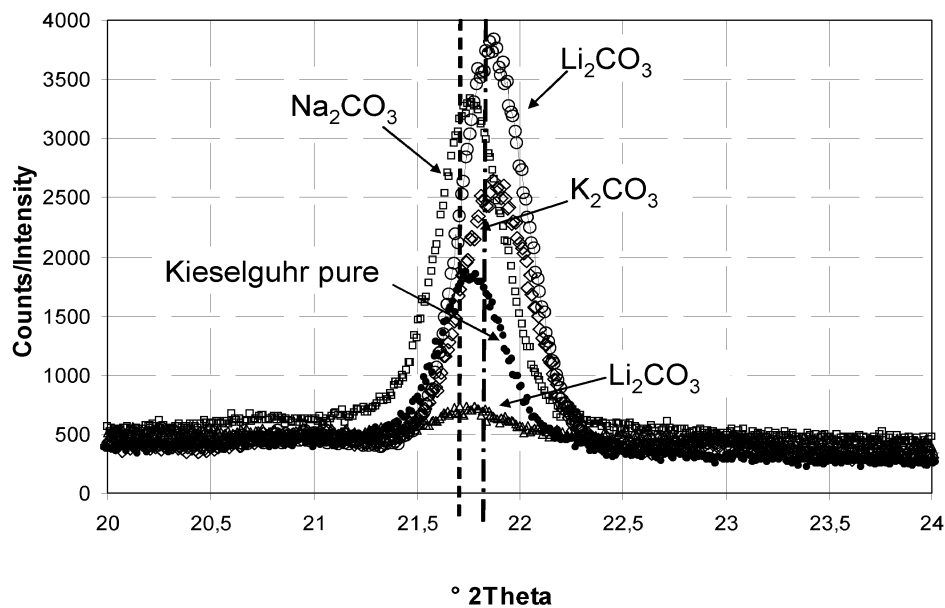
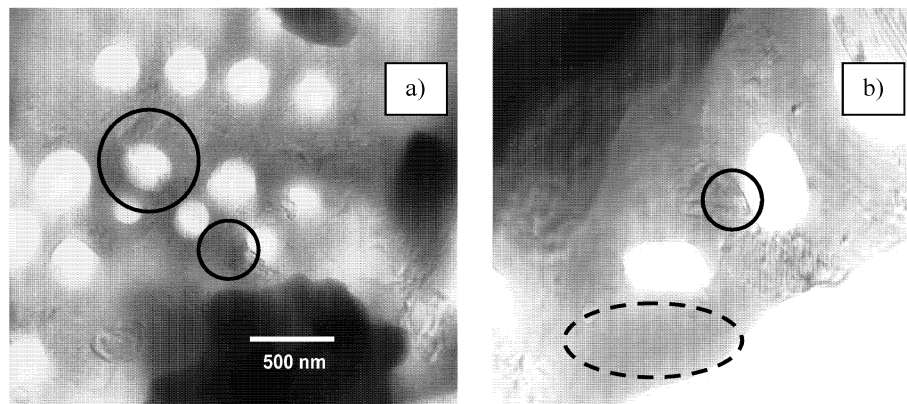


Figure 1: XRD patterns of Kieselguhr with varying flux-component: Influence of flux-agent type on Cristobalite formation during calcination of FN1 Kieselguhr

From practical point of view, potassium or sodium carbonate can be recommended. The influence of these two representatives on the particle surface of calcinated Kieselguhr was investigated in more detail.

Depending on flux-agent type, either whole surface, or only parts of it is covered by new crystals of Cristobalite. It is of peculiar importance to understand two antagonistic

parameters by calcination (modification) of natural Kieselguhr. On the one hand, it is desired to use flux-agent to speed-up the sintering of the pores and to improve the porosity of the particles; on the other hand, flux addition, elevated temperature and longer calcination time lead preferably to the formation of Cristobalite. This problem can however be solved by choosing proper flux-agent and with the selection of appropriate calcination conditions. TEM analysis (Figure 2a) showed the growth of Cristobalite crystals on the bulk surface and also in the mouths of pores (see full circles in Fig. 2a), particularly in the case of sodium carbonate used as a flux agent. Figure 2b depicts an image of potassium carbonate modified Kieselguhr showing less Cristobalite formation and unaffected regions too. Reduced growth rate of Cristobalite with visible crystalline-free parts of the surface can be easily found in Fig. 2b, see full circles. The free (amorphous) surface is marked with dotted ellipse.



*Figure 2: Electron microscopy of FNI Kieselguhr with different flux agents  
a) Sodium carbonate; b) Potassium carbonate*

Another parameter characterizes the quality of final modified Kieselguhr is the porosity. To perform a successful filtration, it is of big benefit to use Kieselguhr particles with different filtration behaviour. Therefore, Kieselguhr with porosity above 4.0 Darcy needs to be used.

Relating achieved porosities of our modified Kieselguhr to the Cristobalite concentration in the final product, only sodium and potassium carbonate can be used (Schleicher et al., 2008). Thus, our further activities are focused on deeper investigation of these two representatives of the flux-agent in industry-like process conditions. For the final decision of the application of either sodium carbonate, or potassium carbonate or a mixture of both, a calcination oven of special construction art has to be used, which allows us an in-situ collection of probes and measurement of axial temperature profiles. The scheme of the unit is given in Figure 3.

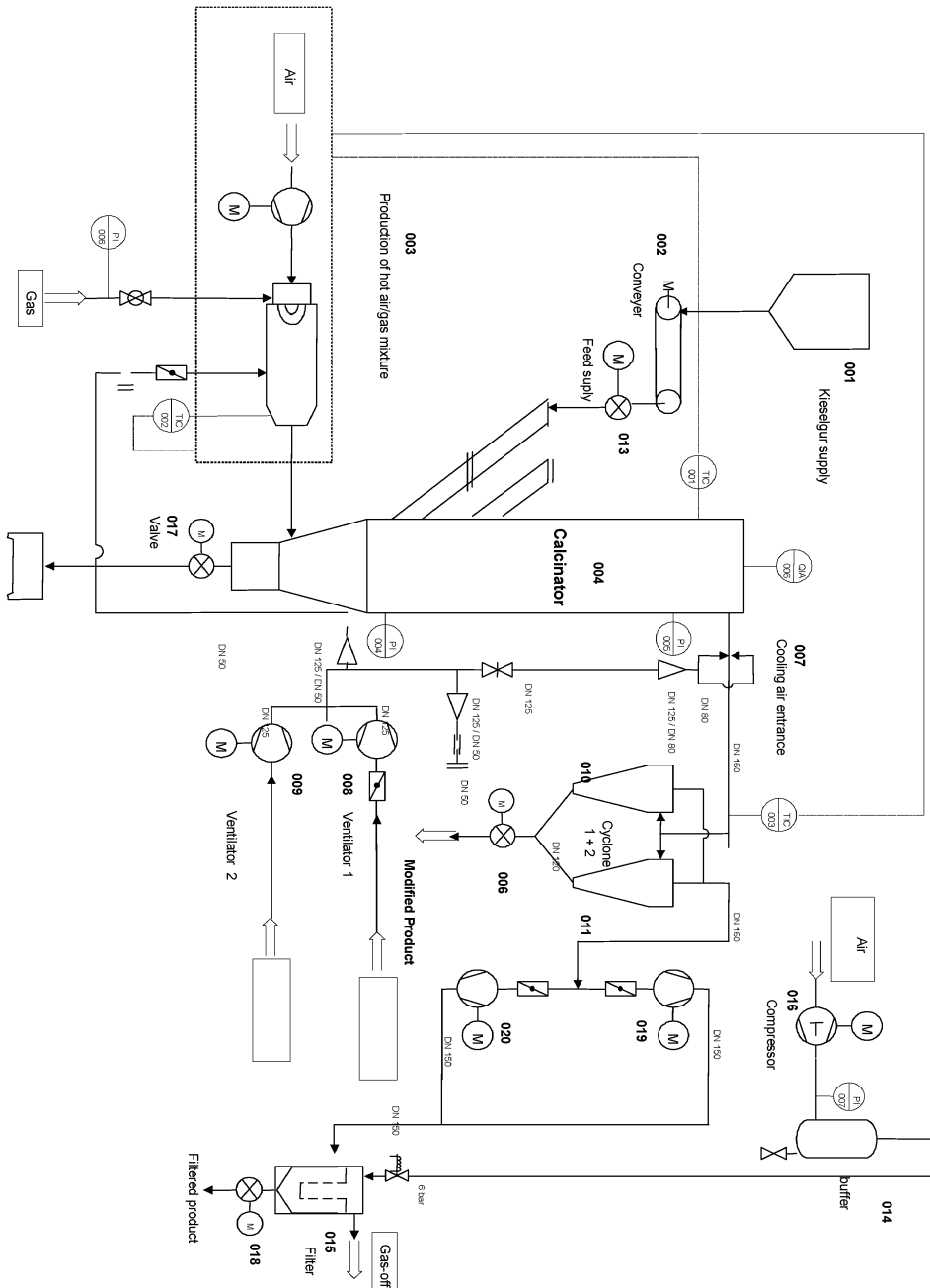


Figure 3: Simplified layout of industrial testing oven unit for calcination of modified Kieselguhr in presence of various flux-agents

#### **4. Conclusions**

The present paper reports a beneficial Kieselguhr calcination processing with potassium carbonate used as flux agent in contrast to the generally accepted meaning that only sodium carbonate can be applied. The addition of potassium carbonate enables to prepare high porosity Kieselguhr with very low concentration of undesired Cristobalite.

#### **5. Acknowledgement**

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