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Influences of the Type of Fluxing Agent during Fluxcalcination of Kieselguhr on Formation of Crystalline Phases, Permeability and Colour

Commercial fluxcalcined kieselguhr or coarse kieselguhr is produced using sodium carbonate as fluxing agent. This coarse kieselguhr contains crystalline structures of silicon dioxide, mainly cristobalite and opal-CT. These crystalline structures are, in respirable form, classified as carcinogenic material and thereby cause concern in occupational health and disposal of spent material. In this paper the influence of the formation of crystalline material during fluxcalcination of kieselguhr using various fluxing agents is described. Additionally characteristics of the kieselguhr samples, concerning the suitability as filter aid have been investigated. Samples were heat treated from 900 °C to 1050 °C for 1h to 4h in a muffle kiln. These samples were analysed via X-ray diffractometry, in order to determine type and content of crystalline material. Based upon these experiments, it was proven that the fluxcalcination of kieselguhr can be accomplished using fluxing agents containing potassium ions. These fluxing agents lead to a coarse kieselguhr which is significantly lowered in crystalline matter, has suitable permeability and wet density and equal colour values compared to commercial fluxcalcined kieselguhr.

Descriptors: kieselguhr, fluxing agent, fluxcalcination, filtration, X-ray diffractometry, cristobalite

1 Introduction

Kieselguhr, diatomaceous earth or diatomite is a sedimentary rock mainly composed of the skeletons of diatoms, a unicellular aquatic plant related to algae. These skeletons consist of opal like, amorphous silica, containing small amounts of microcrystalline structures. Besides the raw material includes organic matter and up to 65 wt. % moisture, small amounts of Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, CaO, and K_2O, depending on its origin. Kieselguhr is a broad term used for thousands of species which occur in various shapes. Their interior is typically hollow and the surface is perforated. Kieselguhr is worldwide used for deep bed filtration processes in the food and beverage industry. Due to its excellent characteristics as high absorptive capacity, surface area and chemical stability, alternative filter aids could not prevail [2, 11, 12, 13, 14].

Prior to using kieselguhr as a filter aid, the raw material has to undergo a conditioning process. Three types of kieselguhr have to be differentiated: dried, calcined, and fluxcalcined. As the raw material can contain up to 65 wt. % moisture, a dehydration of the raw material is essential. Therefore the kieselguhr is treated at temperatures from 300 °C to 400 °C. After drying, the kieselguhr is grinded and classified. This dried kieselguhr can be used as fine kieselguhr for beer filtration, if the raw material is of high purity and has few amounts of organic matter. Calcined kieselguhr is manufactured at temperatures from 800 °C to 1000 °C, typically in rotary kilns. During this heat treatment organic matter is removed and the kieselguhr slightly sinters. Due to this sintering process, the permeability of calcined kieselguhr is heightened. Fluxcalcined kieselguhr is produced at 900 °C to 1200 °C, adding an alkaline flux, generally sodium carbonate, to the kieselguhr. Due to the admixture of the fluxing agent, the melting point of the kieselguhr is significantly lowered. The Permeability of the fluxcalcined or coarse kieselguhr strongly arises and surface area decreases [2, 11, 12, 13, 14]. This guarantees low pressure differences in beverage filtration process. During calcination, and especially the fluxcalcination process, most of the amorphous opal (SiO_2 x nH_2O) in the raw material is transformed into crystalline silica. The appearing crystalline modification of silicon dioxide in calcined and fluxcalcined kieselguhr are: quartz, cristobalite, tridymite, opal-C and opal-CT [2, 15].

The most common crystalline modification of kieselguhr in nature is quartz. Quartz is a tetrahedral framework structure in which Si is 4-coordinated to O atoms, which in turn bridge two Si tetrahedrons to form a framework of tetrahedrons. Two thermal polymorphs of quartz are existent, the high-temperature form, stable only above 573 °C and the low-temperature form. Both forms are of tetrahedral origin. Quartz is considered as chemical inert [9, 15]. Though, quartz can convert to cristobalite at temperatures above 1000 °C, although the reaction is very slow [9].

Cristobalite is the second most common crystalline modification of silicon dioxide, named after its location in Cerro de San Cristobal. Cristobalite is also a tetrahedral framework structure composed of 6-membered rings. Two polymorphs of cristobalite are existent. The high-temperature β-cristobalite is formed out of pure silica at temperatures greater than

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Tables and figures see Appendix

1470 °C. The high-temperature mode is of cubical shape and metabolizes into α-cristobalite, a tetrahedral framework structure at temperatures below 270 °C [2, 9, 15, 16, 17]. Compared to quartz cristobalite has a more open structure and traces of alkali ions may be incorporated in the cages combined with aluminium, substituting the silicon in the framework [15]. At temperatures of 1470 °C cristobalite can be converted into tridymite, if alkaline ions are present. Though, the conversion is very slow [9].

Tridymite is a crystalline form of silicon dioxide that consists of tetrahedrons linked in 6-membered loops, similar but with a different topology than cristobalite [15]. Besides, three polymorphs have been observed. A low-temperature form of monoclinic structure, an orthorhombic structure formed between 163 °C and 250 °C and a hexagonal high-temperature form above 350 °C [9]. Natural tridymite contains small amounts of sodium, and its synthesis is impossible without the presence of an alkali [15].

Beside the amorphous form of opal, two crystalline modification of opal, very similar to cristobalite, are existent. Opal-C is a structure with partial ordering that mimics cristobalite, whereas opal-CT shows some small ordered domains with cristobalite-like and tridymite-like character [15].

Epidemiological studies show that, depending on the cumulative exposition, crystalline silicon dioxide in alveolar form has a significant higher risk of lung cancer compared to amorphous silicon dioxide [4, 5, 6, 7]. This fact initiated the IARC (International Agency for Research on Cancer) to categorize quartz, tridymite and cristobalite as carcinogenic to human [10]. The "Ausschuss für Gefahrstoffe" of the German "Bundesanstalt fuer Arbeitsschutz- und Arbeitsmedizin" classified crystalline silicon dioxide, namely cristobalite and quartz, in alveolar form as carcinogenic to human [3]. Tridymite is, due to non existent epidemiological studies not classified as carcinogenic, though studies claim that tridymite has a similar toxicity to cristobalite, which appears to be even more toxic than quartz [15].

Early studies of Flörke determined the effects of alkali ions on the crystallisation of silicon dioxide. Flörke postulated a correlation between ion radius of the alkine ions and the void volume in the lattice of the crystalline structure. Thus, lithium and sodium can enter the lattice of quartz, potassium can enter the lattice of tridymite, whereas rubidium and caesium advance the formation of cristobalite. In experiments he was able to verify his theory [8]. Venezia and colleagues postulated that lithium and sodium benefit the formation of cristobalite, whereas potassium and caesium only show the transition of amorphous silicon dioxide to cristobalite and tridymite when present in large amounts [17].

Therefore it seems possible to fluxcalinate amorphous kieselguhr under controlled conditions with small amounts of fluxing agents containing potassium, magnesium or calcium without a transformation of amorphous silicon dioxide to cristobalite or other crystalline phases of silicon dioxide. In this study the influence of the fluxing agent on the crystallisation of amorphous kieselguhr was determined. Crystalline modifications have been verified via XRD. Additionally important parameters for beer filtration have been investigated.

2 Material and methods

Raw Materials

For fluxcalcination experiments kieselguhr Celatom FN 1 (Eagle-Pitcher Minerals Inc., Reno, USA) was used. As fluxing agents for fluxcalcination at laboratory scale sodium carbonate (purity > 99.0 %, CAS-Nr.: 497-19-8, Sigma-Aldrich Co., St. Louis, USA), sodium chloride (purity > 99.5 %, CAS-Nr.: 7647-14-5, Sigma-Aldrich Co., St. Louis, USA), disodium hydrogen phosphate (purity > 99.5 %, CAS-Nr.: 7558-79-4, Sigma-Aldrich Co., St. Louis, USA), potassium carbonate (purity > 99.0 %, CAS-Nr.: 584-08-7, Sigma-Aldrich Co., St. Louis, USA), potassium chloride (purity > 99.0 %, CAS-Nr.: 7447-40-7, Sigma-Aldrich Co., St. Louis, USA), dipotassium hydrogen phosphate (purity > 99.0 %, CAS-Nr.: 7758-11-4, Sigma-Aldrich Co., St. Louis, USA), calcium carbonate (purity > 99.0 %, CAS-Nr.: 471-34-1, Sigma-Aldrich Co., St. Louis, USA), calcium chloride dihydrate (purity > 99.0 %, CAS-Nr.: 10035-04-8, Sigma-Aldrich Co., St. Louis, USA), calcium oxide (purity > 96.0 %, CAS-Nr.: 1305-78-8, Riedel-de-Haën, Seelze, Germany), magnesium chloride hexahydrate (purity > 99.0 %, CAS-Nr.: 7791-18-6, Sigma-Aldrich Co., St. Louis, USA) and magnesium oxide (purity > 97.0 %, CAS-Nr.: 1309-48-4, Sigma-Aldrich Co., St. Louis, USA) were used.

For X-ray diffractometry calibration cristobalite standard M 72 (Quarzwerke GmbH, Frechen, Germany) was used. As model coarse kieselguhr Becogur 3500 (E. Begerow GmbH & Co., Langenlonsheim, Germany) came into operation.

Figure 1 displays the XRD-scans of Becogur 3500 and kieselguhr type FN 1. Whereas the XRD-scan of Becogur 3500 shows great amounts of crystalline material, the raw material for fluxcalcination experiments consists mostly of amorphous opal. Beyond small amounts of quartz and opal-CT, as microcrystalline material in the raw material could be verified.

Fluxcalcination

As the cations of the fluxing agents differ in molar mass, it is essential to admix the same amount of cations, which are responsible for the sintering process, to the kieselguhr. Using the same molar ratio of cations, comparability of the different fluxing agents can be assured. The admixture of fluxing agent to the kieselguhr was calculated using following equation:

$$W = \left[a - \left(\frac{a*b}{100} \right) \right] * c * d * e \tag{1}$$

W = net weight of fluxing agent [g]

a = net weight of kieselguhr [g]

b = loss due to burning of kieselguhr [mass.-%]

c = amount of cations [mol cations/g kieselguhr]

d = molar mass of the fluxing agent [g/mol]

e = valence factor, (1 if valence of cation and anion are equal e.g. NaCl, or 0.5 if valence of the anion is double compared to the cation e.g. Na_2CO_3)

To avoid inhomogeneous mixtures of fluxing agent and kieselguhr at laboratory scale, the fluxing agents were admixed in aqueous state. Therefore the fluxing agents were dissolved in 300 ml aqua distillate. Afterwards 100 g kieselguhr FN 1 have been admixed to the aqueous solution. During the drying process at 75 °C for 72 h, the mixtures was stirred every 24 h. Finally the dry material was grinded to particle sizes smaller than 500 µm.

Mixtures of kieselguhr and fluxing agents in concentrations from $1.887 * 10^{-4}$ [mol cations/g kieselguhr] to $1.132 * 10^{-3}$ [mol cations/g kieselguhr] came into operation. The samples have been heat treated in ceramic pots in a chamber furnace type KK 80 (Linn High Therm GmbH, Eschenfelden, Germany) at temperatures form 900 °C to 1050 °C. The duration of heat treatment varied between 1 h and 4 h. After heat treatment the samples were cooled down to ambient temperature in an exsiccator.

X-ray diffractometry

Crystalline modifications of silicon dioxide were detected via X-ray diffractometry. X-ray diffractometry is based upon the fact that monochrome X-radiation is diffracted by crystalline matter. The diffraction of X-radiation is caused by interferences of the reflected beams.

X-radiation can be detected via radiographic films, counter tubes or semiconductor detectors. Bragg's law determines the interference of X-radiation according to equation 2:

$$n * \lambda = 2 * d * \sin\theta \qquad (2)$$

n = coefficient of reflexion

λ = wavelength of the beam [Å]

d = spacing between diffracting planes [Å]

θ = angle between beam an diffraction plane [°]

According to Bragg's law the spacing between diffracting planes, knowing the wavelength of the beam, the angle between X-radiation source and sample and angle between sample and X-ray detector, can be calculated. Knowing the spacing between diffracting planes the sample can be identified.

For identifying crystalline matter of silicon dioxide an X-ray diffractometer type PW 1050/70 (Philips, The Netherlands) has been used. Following adjustments have been chosen:

CoK_α-radiation: λ = 1.788965 Å (X-ray Source: PW 2236/20, PANalytical)

Tube voltage: 40 kV

Tube current: 30 mA

Detector: Proportional counter

Divergence slit: 1°

Monochromator: Graphite Monochromator

Increment: 0.02°

Test time: 2 sec

As the main peaks of crystalline modifications of silicon dioxide appear between 24° 2θ and 26° 2θ a measurement range from 23° 2θ to 27° 2θ was sufficient.

Permeability and wet density

Permeability and wet density were measured according to MEBAK [1]. Therefore an aqueous solution containing 4 g kieselguhr was mixed. Afterwards this suspension was sucked through a cotton filter cloth (National Filter Media Style 1120 065 03) using a vacuum pump. In the process the kieselguhr formed a consistent filter cake on the surface of the filter cloth. As soon as the vacuum was in a steady state the time in which 20 ml water passed the filter cake and the filter cloth was measured. Finally the height of the filter cake was measured. This procedure was performed three times. Permeability and wet density were calculated using equation 3 and 4:

$$\beta = \frac{V * \eta * h}{t * A * \Delta P} \qquad (3)$$

β = permeability [Darcy]

V = filtrate volume [ml]

η = viscosity of the liquid [cP]

h = height of the filter cake [cm]

t = time [s]

A = filter surface [cm²]

ΔP = pressure difference [bar]

$$p_N = \frac{m}{A * h * 0.001} \qquad (4)$$

p_N = wet density [g/l]

h = height of the filter cake [cm]

A = filter surface [cm²]

m = net weight of kieselguhr [g]

The measurement accuracy of permeability is ± 5.0 mDarcy for values from 40 mDarcy to 100 mDarcy, ± 20.0 mDarcy for values from 180 mDarcy to 400 mDarcy and ± 100.0 mDarcy for values from 1000 mDarcy to 1500 mDarcy. The measurement accuracy of wet density is ± 3.0 g/l.

Colour

Colour measurement of the kieselguhr samples was performed using a tristimulus colorimeter type Chromameter Cr-300 (Konica Minolta Sensing Europe B.V., Nieuwegein, The Netherlands). During the measurement, the light reflected by the sample is separated into its red, green and blue parts and its intensity is measured. Using the software Chroma Magic the intensity values were calculated into the CIE XYZ Colour Space. In order to get information about brightness, hue and colour saturation, the values of the CIE XYZ Colour Space have been transformed to the CIE L*a*b colour space. The L-value describes brightness (0 = black, 100 = white). Red is described by positive a-values and green by negative a-values. The b-value characterises yellow (positive values) and blue (negative values). The colour measurement was performed ten times. The accuracy of the measurement is 0.8 % of the mean value.

3 Results and Discussion

First of all, fluxcalcination at laboratory scale using sodium carbonate as conventional fluxing agent was performed in order to examine the formation process of crystalline silicon dioxide matter. Mixtures of kieselguhr and sodium carbonate in concentrations from $1.887 * 10^{-4}$ [mol cations/g kieselguhr] to $1.132 * 10^{-3}$ [mol cations/g kieselguhr] came into operation, in order to investigate the influence of the fluxing agent's concentration. To analyse the influence of temperature and time on the formation of crystalline silicon dioxide matter the samples were treated at 900 °C, 950 °C, 1000 °C and 1050 °C for 1 h, 2 h and 4 h.

Calcination without fluxing agent

Figure 2 shows the XRD-scans of kieselguhr type FN 1 fluxcalcined without fluxing agent at 1000 °C for 1 h, 2 h and 4 h. By means of the position of the appearing peaks the crystalline structure can be identified. The main peaks of the crystalline modifications of silicon dioxide appear in the range between 24.3° 2θ and 25.64° 2θ (quartz: 24.3° 2θ, tridymite: 25.2° 2θ, opal-CT: 25.20° 2θ – 25.39° 2θ, cristobalite: 25.55° 2θ and opal-C: 25.64° 2θ). The area beneath the peaks is a quantity for the amount of crystalline matter.

Figure 2 proves that even without an admixture of fluxing agent a formation of crystalline structures of silicon dioxide occurred. Though, formation of crystalline matter occurred faster when fluxing agents have been admixed. Regarding the sample heat treated for one hour, still no formation of crystal silicon dioxide could be verified. Heightening the duration of heat treatment up to two hours resulted in a beginning formation of crystalline structures. This effect was advanced at a heat treatment of 4 h. This XRD-scan shows clearly the formation of crystalline material. The verified structure was disordered opal-CT. Still its concentration was low.

Sodium carbonate as fluxing agent

Figure 3 shows the influence of the fluxing agent's concentration on the formation of crystalline matter. Increasing concentrations of fluxing agent led on the one hand to more crystalline material in the kieselguhr and on the other hand to more regular crystal structures. In the samples with sodium carbonate concentrations from $1.887 * 10^{-4}$ [mol cations/g kieselguhr] to $5.661 * 10^{-4}$ [mol cations/g kieselguhr] the formation of crystalline structures was still low. The formed crystalline matter appears to be disordered opal-CT. Increasing concentrations of the fluxing agent led to greater concentrations of crystalline matter. Additionally the main peaks of the crystalline structures appeared at higher angles, which points at well ordered opal-CT. However, the formation of cristobalite could not be verified in any sample.

The influence of temperature was akin to the influence of the fluxing agent's concentration on the formation of crystalline silicon dioxide. Kieselguhr type FN 1 samples with fluxing agent concentration of $9.435 * 10^{-4}$ [mol/g kieselguhr] have been fluxcalcinced for two hours at four different temperatures (Fig. 4). An increase of temperature from 900 °C to 1000 °C, in steps of 50 K, resulted almost in a doubling of crystalline matter in the kieselguhr, each time. Further raise of temperature to 1050 °C had almost no influence on the amount of crystalline silicon dioxide, but on the crystal type. Every temperature elevation led to more regular crystal structures. Whereas the crystal structure of the samples fluxcalcined at 900 °C and 950 °C was disordered opal-CT, a further raise of temperature resulted in well order opal-CT structures.

Compared to the influence of temperature and fluxing agent's concentration the influence of calcination duration on the formation of crystalline matter seemed to be low. Figure 5 shows the XRD-scans of kieselguhr type FN 1 samples with fluxing agent concentration of $9.435 * 10^{-4}$ [mol/g kiesel-guhr] fluxcalcined at 1000 °C for 1, 2 and 4 hours. The amount of crystalline silicon dioxide, as well as the crystal structure after 1 and 2 hours of heat treatment was equal. This means that the formation of crystalline material was already finished after one hour heat treatment. This fact was supported by the XRD-scan of the sample which was heat treated for 4 hours. The enhancement of duration had almost no influence.

Sodium chloride as fluxing agent

Figure 6 shows the XRD-scans of kieselguhr type FN 1, fluxcalcined with sodium chloride as fluxing agent in different concentrations. Sodium chloride also enhanced the formation of crystalline matter, but to a minor degree compared to sodium carbonate. Concentrations of sodium chloride up to $5.661 * 10^{-4}$ [mol/g kieselguhr] caused almost no formation of crystalline material. Heightening the fluxing agent's concentration led to formation of disordered opal-CT. Further increas-ing of concentration had marginal influence on the amount of crystalline matter, but on the regularity of opal-CT.

Disodium hydrogen phosphate as fluxing agent

XRD-scans of kieselguhr type FN 1, fluxcalcined with different concentrations of disodium hydrogen phosphate as fluxing agent are displayed in figure 7. The tendency of kieselguhr to form crystalline material, if disodium hydrogen phosphate was admixed is comparable to the formation of crystalline matter if sodium carbonate was admixed as fluxing agent. At high concentrations of the fluxing agent (1.132 * 10^{-3} [mol/g kieselguhr]) the formation of crystalline silica was even greater.

Potassium carbonate as fluxing agent

Figure 8 shows the XRD-scans of kieselguhr type FN 1, fluxcalcined with potassium carbonate as fluxing agent fluxcalcined at 1000 °C for 2 h. The affinity to form crystalline matter using potassium carbonate was significant lower, compared to fluxing agents containing sodium. Samples containing up to 5.661 * 10^{-4} [mol cations/g kieselguhr] potassium sodium carbonate showed no formation of crystal structures. Increasing the concentration led to formation of disordered opal-CT. Still its concentration in the fluxcalcined kieselguhr was low.

Potassium chloride as fluxing agent

Using potassium chloride as fluxing agent enhanced the effect observed when potassium carbonate came into operation (Fig. 9). An admixture up to 7.548 * 10^{-4} [mol cations/g kieselguhr] to kieselguhr type FN 1 showed no formation of crystalline matter at calcination conditions of 1000 °C for 2 h. Raising the concentration of potassium chloride up to 9.435 * 10^{-4} [mol cations/g kieselguhr] the formation of crystal structures began. Disadvantageous compared to potassium carbonate as fluxing agent was the formation of hydrogen chloride gas during the calcination process.

Dipotassium hydrogen phosphate as fluxing agent

Figure 10 shows the XRD-scans of kieselguhr type FN 1, fluxcalcined with dipotassium hydrogen phosphate as fluxing agent fluxcalcined at 1000 °C for 2 h. The tendency of the kieselguhr-fluxing-agent-mixtures to form crystalline structures was comparable to the admixture of potassium chloride to kieselguhr type FN 1. Advantageous was that the use of dipotassium hydrogen phosphate led to no formation of hydrogen chloride gas.

Calcium carbonate as fluxing agent

Figure 11 shows the XRD-scans of kieselguhr type FN 1, fluxcalcined with calcium carbonate as fluxing agent fluxcalcined at 1000 °C for 2 h. In contrast to fluxing agents containing sodium or potassium, the concentration of the fluxing agent's admixture to the kieselguhr seemed to have no influence on the formation of crystalline structures. The amount and type of crystalline structures in the different samples was almost equal.

Calcium chloride dihydrate as fluxing agent

The use calcium chloride dihydrate as fluxing agent resulted in the greatest formation of crystalline matter in the fluxcalcined kieselguhr. XRD-scans are displayed in figure 12. Even at low concentrations of the fluxing agent (1.887 * 10^{-4} [mol cations/g kieselguhr]) a formation of crystalline structures of silicon dioxide could be observed. Whereas concentrations up to 5.661 * 10^{-4} [mol cations/g kieselguhr] led to formation of disordered opal-CT, a rise of the fluxing agent's concentration advanced the formation of regular crystal structures. In the samples containing 9.435 * 10^{-4} and 1.132 * 10^{-3} [mol cations/g kieselguhr] calcium chloride dehydrate, the formation of cristobalite could be verified via XRD. Beyond, the use of calcium chloride dehydrate led to formation of chloride hydrogen gas, like the use of potassium chloride.

Calcium oxide as fluxing agent

Figure 13 shows the XRD-scans of kieselguhr type FN 1, fluxcalcined with calcium oxide as fluxing agent at 1000 °C for 2 h. The XRD-scans reflect the effects observed when calcium carbonate was used as fluxing agent. The concentration of the fluxing agent's admixture to the kieselguhr had low influence on the formation of crystal structures. In general the formation of crystalline matter was low.

Magnesium chloride hexahydrate as fluxing agent

Figure 14 shows the XRD-scans of kieselguhr type FN 1, fluxcalcined with magnesium chloride hexahydrate as fluxing agent at 1000 °C for 2 h in chamber furnace type KK 80. The use of magnesium chloride hexahydrate as fluxing agent resulted in low concentrations of disordered crystalline matter (opal-CT) in the fluxcalcined kieselguhr. Regarding the influence of the fluxing agent's concentration the amount of magnesium chloride has almost no effect on the formation of crystalline matter.

Magnesium oxide as fluxing agent

The use magnesium oxide as fluxing agent resulted in very low concentrations of crystalline structures of silicon dioxide in the fluxcalcined kieselguhr. XRD-scan are displayed in figure 15. Interestingly, the formation of crystalline structures occurred at low concentration's of the fluxing agent (up to 7.548 * 10^{-4} [mol cations/g kieselguhr]). Raising the concentration of the fluxing agent (up to 9.435 * 10^{-4} [mol cations/g kieselguhr]) inhibited the formation of crystalline silicon dioxide in the fluxcalcined kieselguhr. This behaviour was vice versa to all other fluxing agents. Again the fluxcalcination was carried out at 1000 °C for 2 h.

Permeability and Wet Density

In order to investigate the suitability as coarse kieselguhr for beer filtration, the permeability and wet density of the fluxcalcined kieselguhr samples was measured. The untreated material kieselguhr type FN 1 had a permeability of 48.2 mDarcy [± 5.0 mDarcy] and a wet density of 364.8 g/l [± 3.0 g/l]. As model coarse kieselguhr Becogur 3500 came into account. The permeability of Becogur 3500 was 1370.2 mDarcy [± 100.0 mDarcy] and the wet density 376.6 g/l [± 3.0 g/l]. Table 1 shows the permeabilities and wet densities of kieselguhr type FN 1 samples, fluxcalcined with different fluxing agents at a fluxing agent's concentration of 9.435 * 10^{-4} [mol cations/g kieselguhr] at 1000 °C for 2 h in chamber furnace type KK 80. The table displays the mean value of the triple measurement, as well as the difference of the permeability and wet density of the samples compared to Becogur 3500. At first, permeability and wet density of Becogur 3500 are registered.

Regarding the results, the best permeabilities have been achieved using dipotassium hydrogen phosphate, followed by disodium hydrogen phosphate, sodium carbonate, potassium carbonate, and potassium chloride. Fluxing agents like calcium carbonate, magnesium oxide or magnesium chloride hexahydrate led to low permeabilities in the fluxcalcined kieselguhr. This fact leads to the conclusion, that these fluxing agents are not able to lower the melting point of the kieselguhr significantly. Increasing the temperature will probably lead to acceptable permeabilities, combined with high amounts of crystalline structures. The wet densities of the samples fluxcalcined with dipotassium hydrogen phosphate, potassium carbonate, sodium carbonate, potassium chloride and disodium hydrogen phosphate shift in the wet density range of Becogur 3500. When potassium carbonate was used as fluxing agent, the wet density of the kieselguhr sample was fractionally greater.

Compared to Becogur 3500 these permeabilities are partly low (e.g. potassium carbonate as fluxing agent), due to the differing production technique. Usually coarse kieselguhr is produced in rotation kilns that guarantee a continuous mixing of kieselguhr and fluxing agent. In these experiments the kieselguhr-fluxing-agent-mixture was fluxcalcined in a static process in a chamber furnace in melting pots. Result is that the permeabilities of these samples are generally lower.

Colour

Since kieselguhr is used as extender in the painting industry, its suitability as filler in paint has to be investigated. Therefore the colour of the fluxcalcinated kieselguhr is of especial importance.

Table 2 shows the L*a*b*-values kieselguhr type FN 1 samples, fluxcalcined with different fluxing agents at a fluxing agent's concentration of 9.435 * 10^{-4} [mol cations/g kieselguhr] at 1000 °C for 2 h. The table displays the mean value of the tenfold measurement, as well as the difference of the L*a*b*-values of the samples compared to Becogur 3500. At first, the L*a*b*-values of Becogur 3500 are registered.

Regarding the results of the colour measurement, only few fluxing agents are able to produce fluxcalcined kieselguhr suitable for the paint industry. These fluxing agents are dipotassium hydrogen phosphate, followed by sodium carbonate, potassium chloride, sodium chloride and disodium hydrogen phosphate. Most of the samples showed great red values, especially fluxing agents containing calcium or magnesium.

4 Conclusion

Regarding the results, only few fluxing agents are suitable for the fluxcalcination of kieselguhr in order to produce a coarse kieselguhr that is reduced in crystalline matter, has adequate permeabilities and wet densities, as well as a suitable colour. The fluxcalcination experiments described above have proven that, fluxing agents containing potassium are suitable for fluxcalcination of kieselguhr, in particular. The best results have been achieved using dipotassium hydrogen phosphate as fluxing agent. The analysis has proven that these kieselguhr samples were significantly reduced in crystalline matter and had colour values and wet density equal to commercial coarse kieselguhr. The permeability was even higher compared to Becogur 3500. This verifies that fluxing agents containing potassium sufficiently lower the melting point of kieselguhr and avoid the formation of crystalline structures, simultaneously. The formation of crystalline matter is avoided due to the bigger ion size of potassium compared to sodium. Second best results have been achieved using potassium carbonate as fluxing agent, though colour values, permeability and wet density have been lower, compared to dipotassium hydrogen phosphate.

Using fluxing agents containing sodium for the fluxcalcination of kieselguhr led to a product that had adequate permeabilities, wet densities and colour values, but although contained large amounts of crystalline structures. This is determined by the ion size of sodium, which perfectly fits in the crystal lattice of the crystalline modifications of silicon dioxide.

Fluxing agents containing magnesium or calcium were not suitable for fluxcalcination of kieselguhr, as the ability to reduce the melting point of the kieselguhr sufficiently is lacking.

These scientific findings, gained at laboratory scale, will be the base for ongoing fluxcalcination experiments at technical scale in a rotary tube kiln.

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Appendix

Table 1 Permeability and wet density of kieselguhr type FN 1 fluxcalcined at 1000 °C for 2 h with different fluxing agents at concentration of 9.435 * 10^{-4} [mol cations/g kieselguhr]

Type of Fluxing Agent	Permeability		Wet Density	
	Mean value [mDarcy]	Delta [mDarcy]	Mean value [g/l]	Delta [g/l]
Becogur 3500	1370.2	–	376.6	–
without	146.2	1224.0	315.8	60.8
Na_2CO_3	915.3	454.9	349.2	27.4
NaCl	528.3	841.9	351.7	24.9
Na_2HPO_4	1440.9	–70.7	340.9	35.7
K_2CO_3	767.5	602.7	431.5	–54.9
KCl	599.0	771.2	400.6	–24.0
K_2HPO_4	1535.0	–164.8	373.1	3.5
$CaCO_3$	371.1	999.1	331.3	45.3
$CaCl_2$ x 2 H_2O	461.5	908.7	380.4	–3.8
CaO	450.1	920.1	318.9	57.7
$MgCl_2$ x 6 H_2O	260.5	1109.7	447.4	–70.8
MgO	191.6	1178.6	343.8	32.8

Table 2 L*a*b*-values of kieselguhr type FN 1 fluxcalcined at 1000 °C for 2 h with different fluxing agents at concentration of 9.435 * 10^{-4} [mol cations/g kieselguhr]

Type of Fluxing Agent	Colour					
	L*		a*		b*	
	Mean value	Delta	Mean value	Delta	Mean value	Delta
Becogur 3500	95.74	–	0.26	–	2.41	–
without	85.93	9.81	5.99	–5.73	20.25	–17.84
Na_2CO_3	92.69	3.05	2.28	–2.02	3.99	–1.58
NaCl	92.71	3.03	2.65	–2.39	5.20	–2.79
Na_2HPO_4	93.75	1.99	0.46	–0.20	7.60	–5.19
K_2CO_3	88.16	7.58	5.11	–4.85	8.30	–5.89
KCl	93.11	2.63	2.81	–2.55	5.64	–3.23
K_2HPO_4	94.96	0.78	1.12	–0.86	4.18	–1.77
$CaCO_3$	85.60	10.14	6.49	–6.23	19.03	–16.62
$CaCl_2$ x 2 H_2O	94.73	1.01	-1.47	–1.21	13.02	–10.61
CaO	86.39	9.35	6.18	–5.92	15.15	–12.74
$MgCl_2$ x 6 H_2O	87.02	8.72	3.46	–3.20	7.77	–5.36
MgO	87.89	7.85	5.39	–5.13	16.14	–13.73

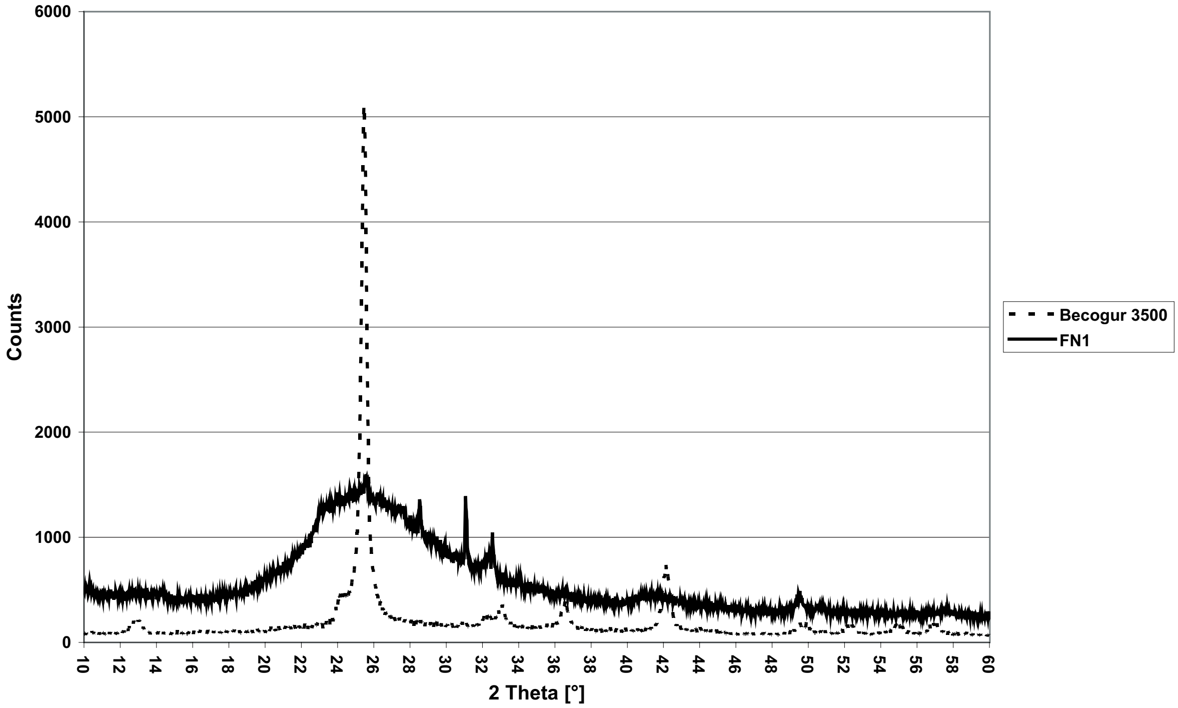

Fig. 1 XRD-scan of kieselguhr type FN 1 and Becogur 3500

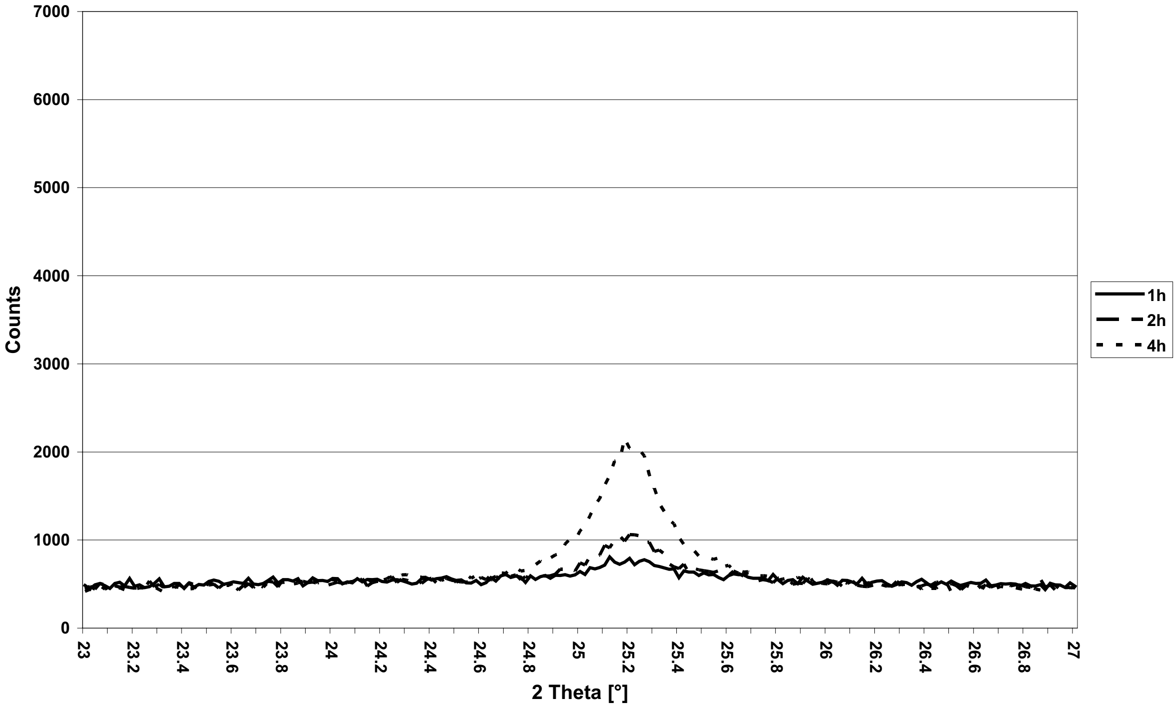

Fig. 2 XRD-scan of kieselguhr type FN 1 calcined without fluxing agent at 1000 °C for 1, 2 and 4h

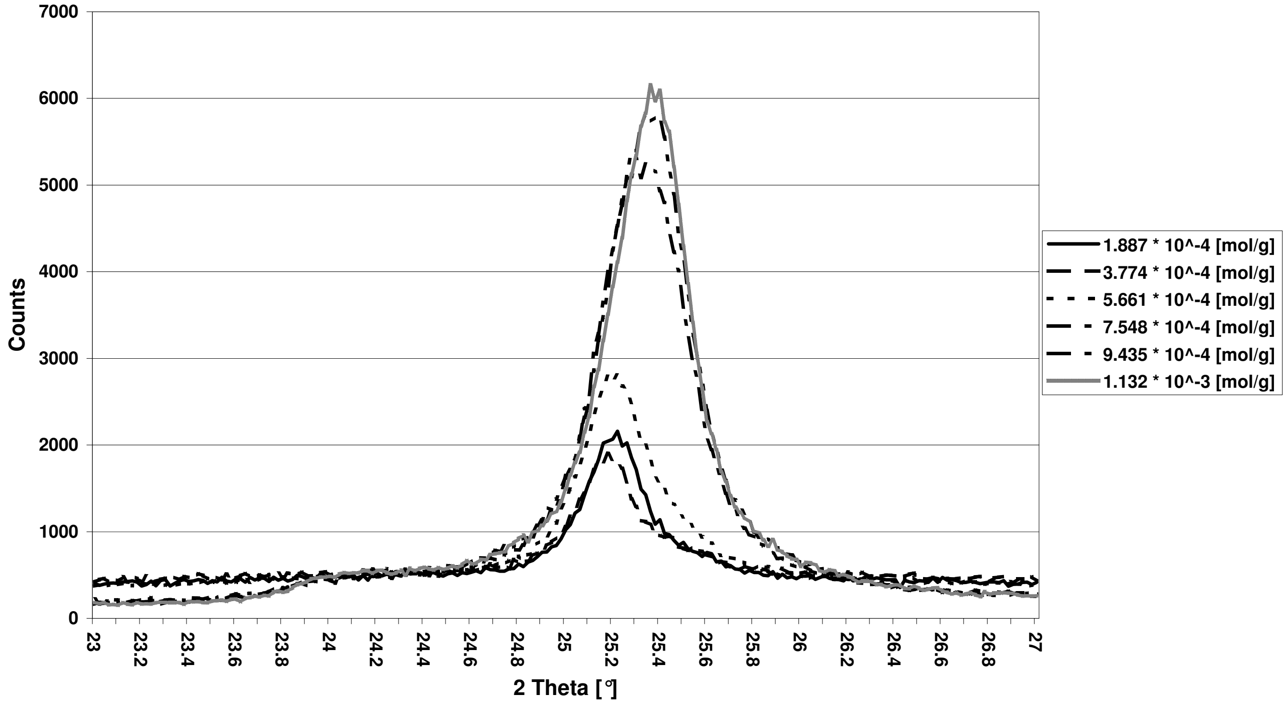

Fig. 3 XRD-scan of kieselguhr type FN 1 fluxcalcined with Na_2CO_3 at different concentrations at 1000 °C for 2 h

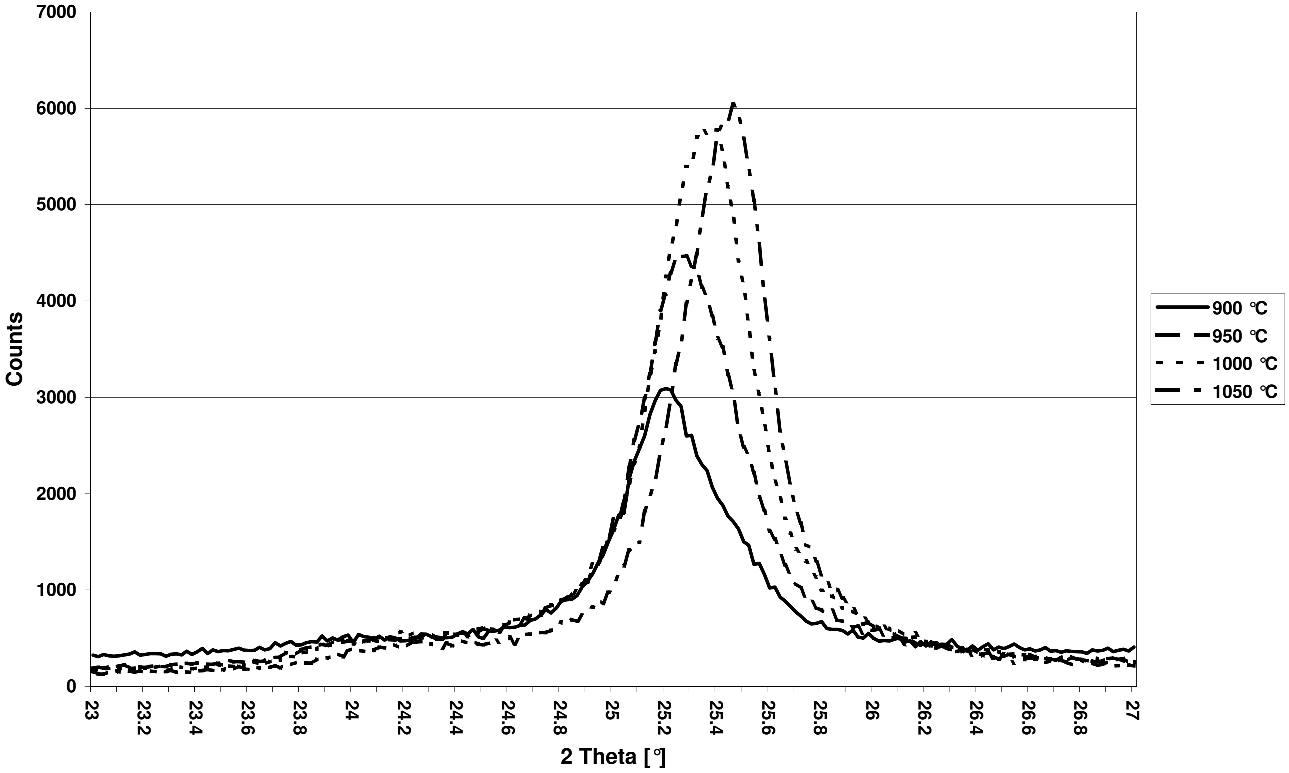

Fig. 4 XRD-scan of kieselguhr type FN 1 fluxcalcined with 9.435 * 10^{-4} [mol/g kieselguhr] Na_2CO_3 at different temperatures for 2 h

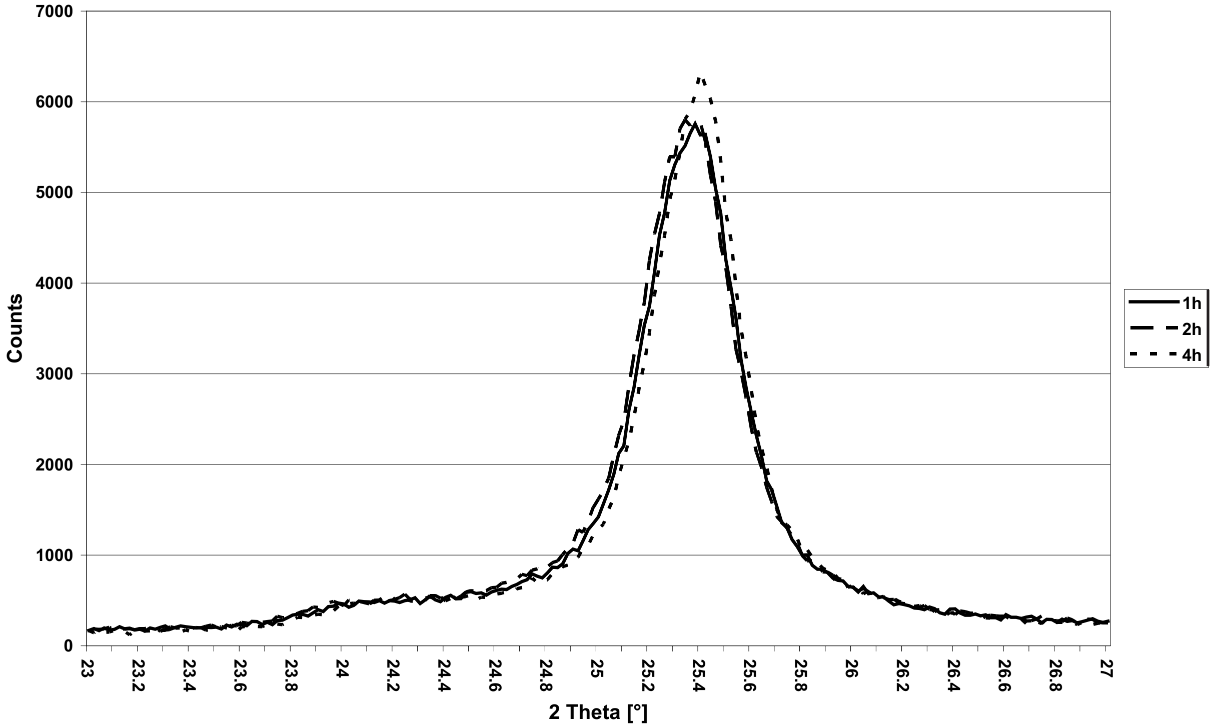

Fig. 5 XRD-scan of kieselguhr type FN 1 fluxcalcined with 9.435 * 10^{-4} [mol/g kieselguhr] Na_2CO_3 at 1000 °C for 1, 2 and 4 h

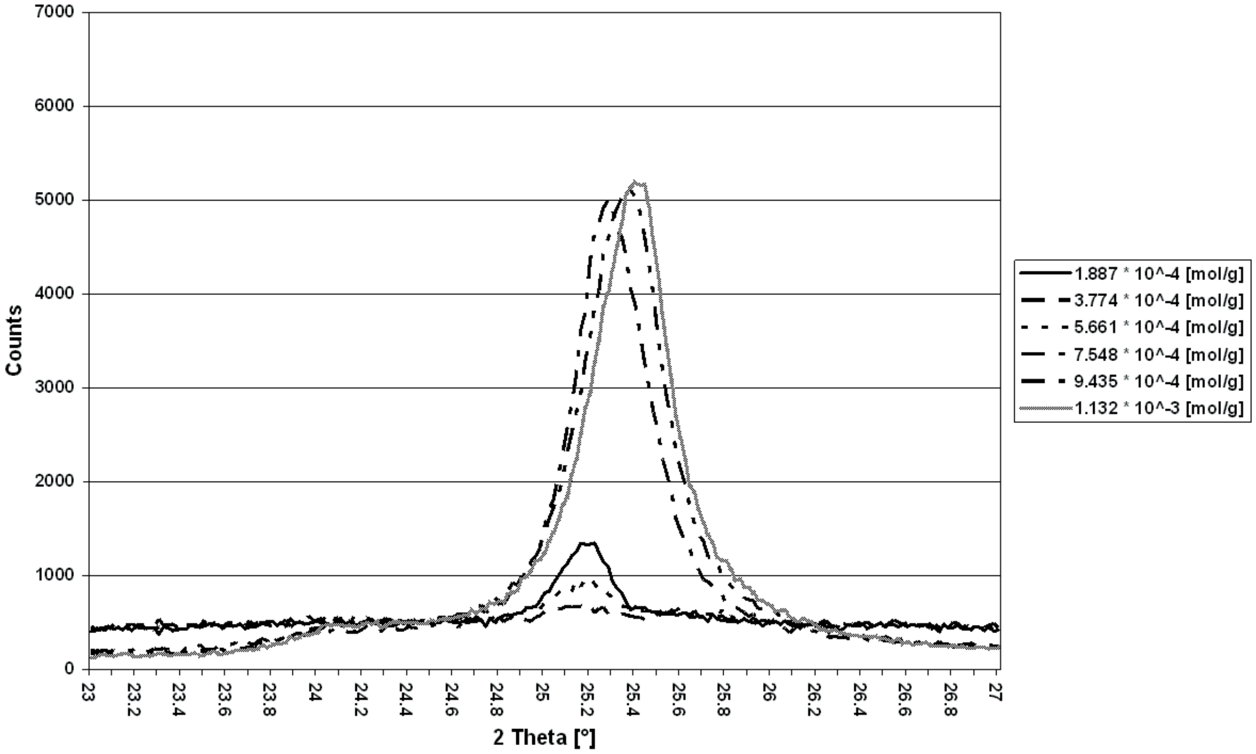

Fig. 6 XRD-scan of kieselguhr type FN 1 fluxcalcined with NaCl at different concentrations at 1000 °C for 2 h

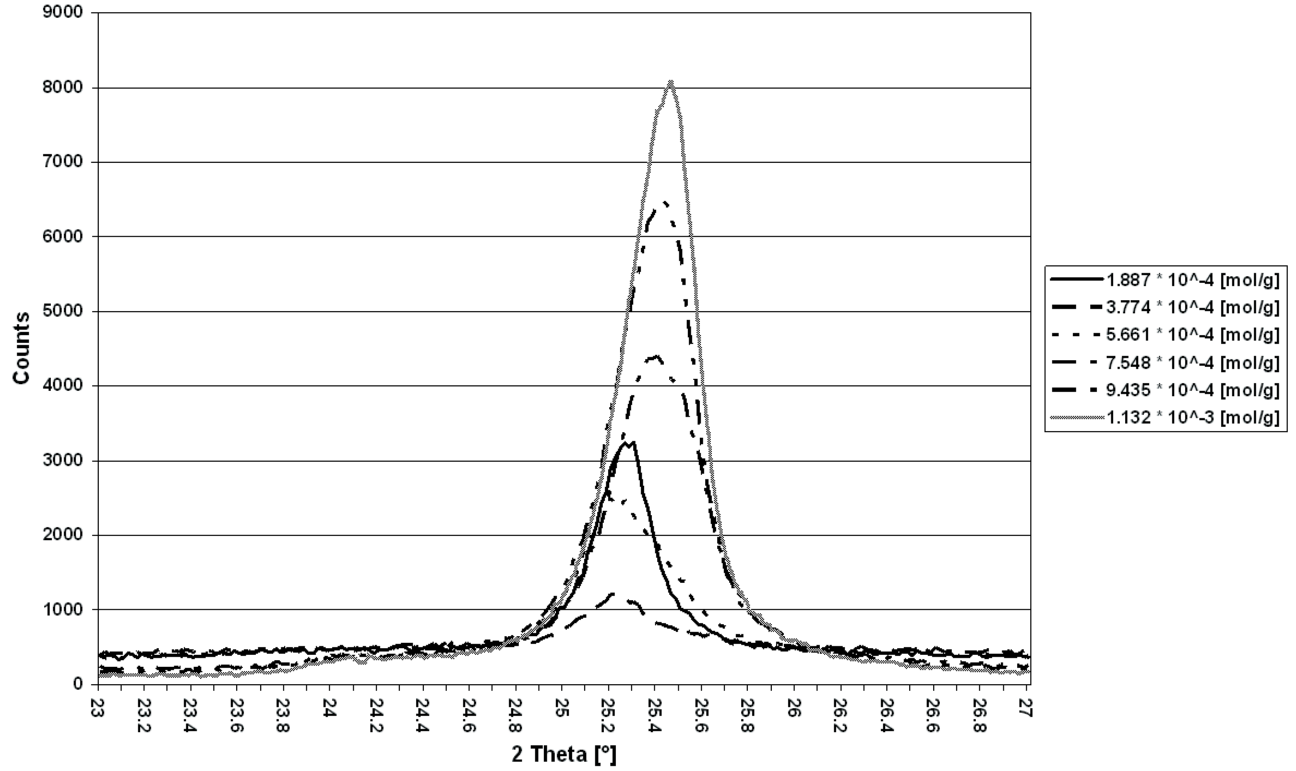

Fig. 7 XRD-scan of kieselguhr type FN 1 fluxcalcined with Na_2HPO_4 at different concentrations at 1000 °C for 2 h

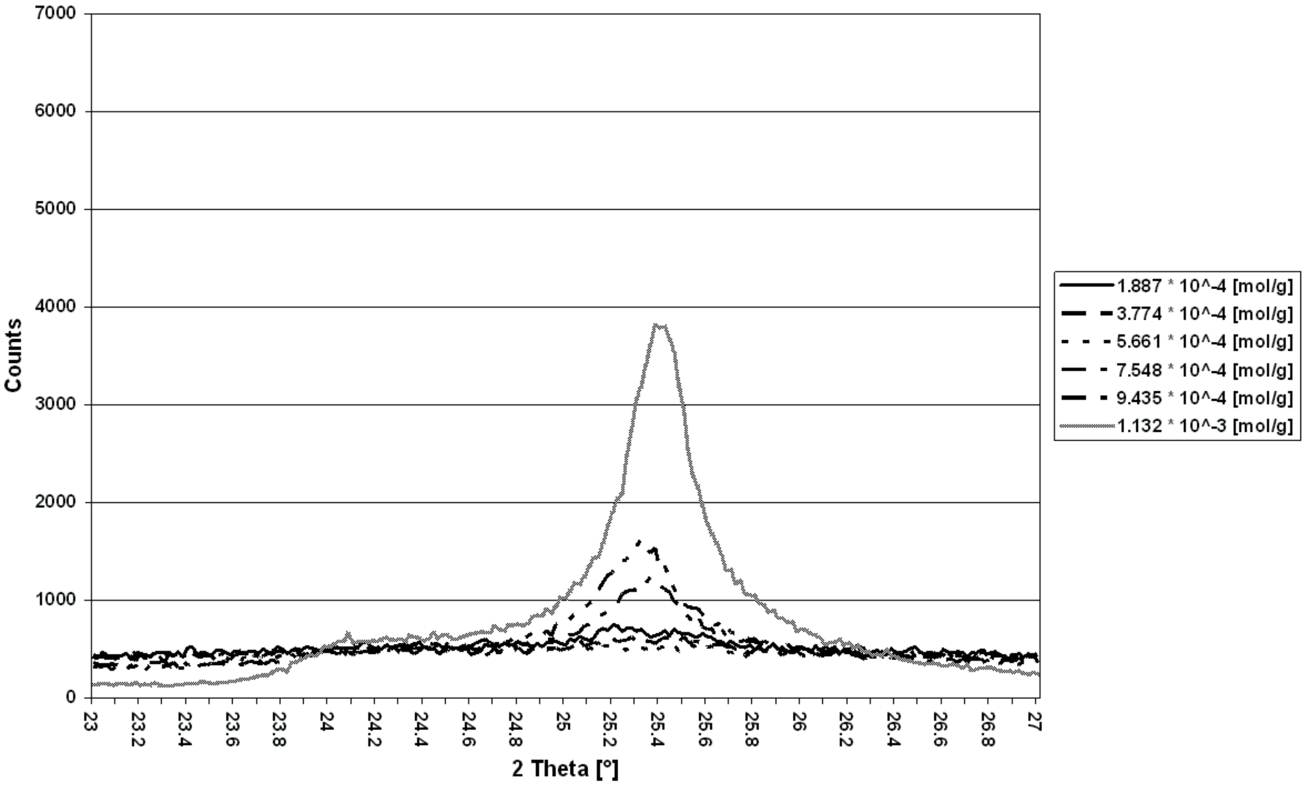

Fig. 8 XRD-scan of kieselguhr type FN 1 fluxcalcined with K_2CO_3 at different concentrations at 1000 °C for 2 h

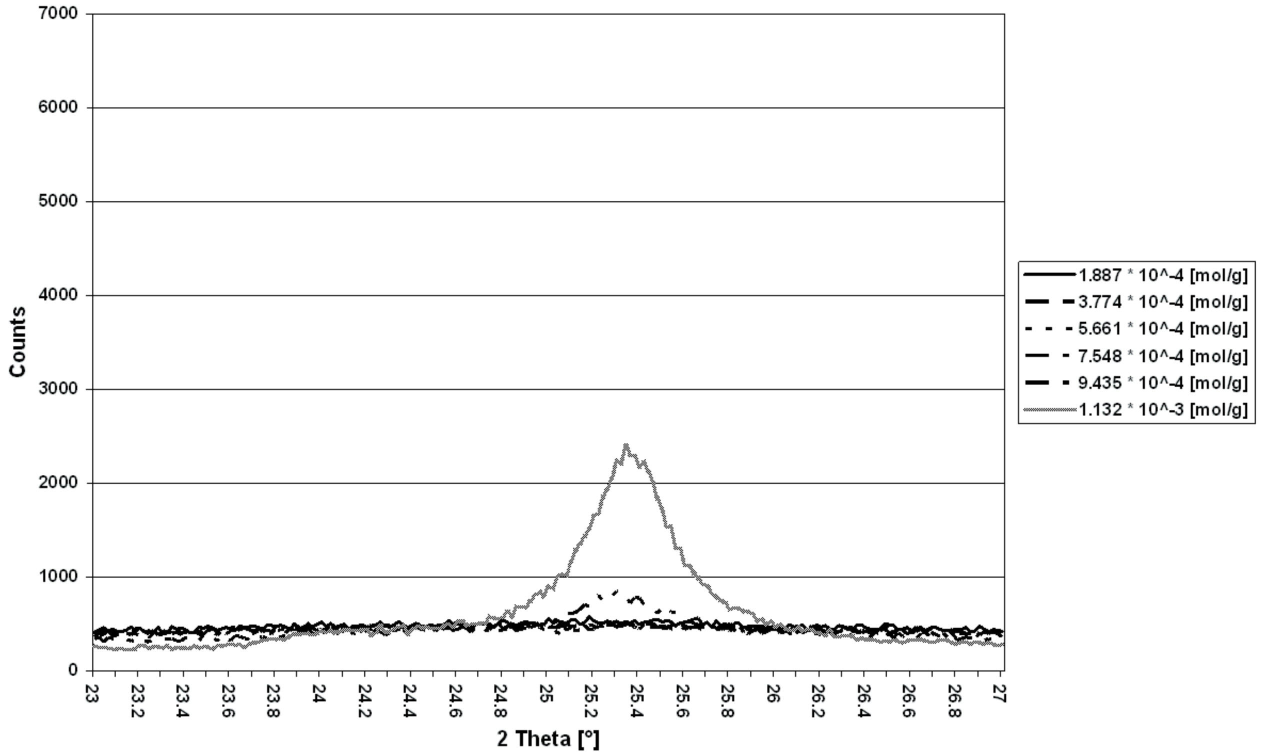

Fig. 9 XRD-scan of kieselguhr type FN 1 fluxcalcined with KCl at different concentrations at 1000 °C for 2 h

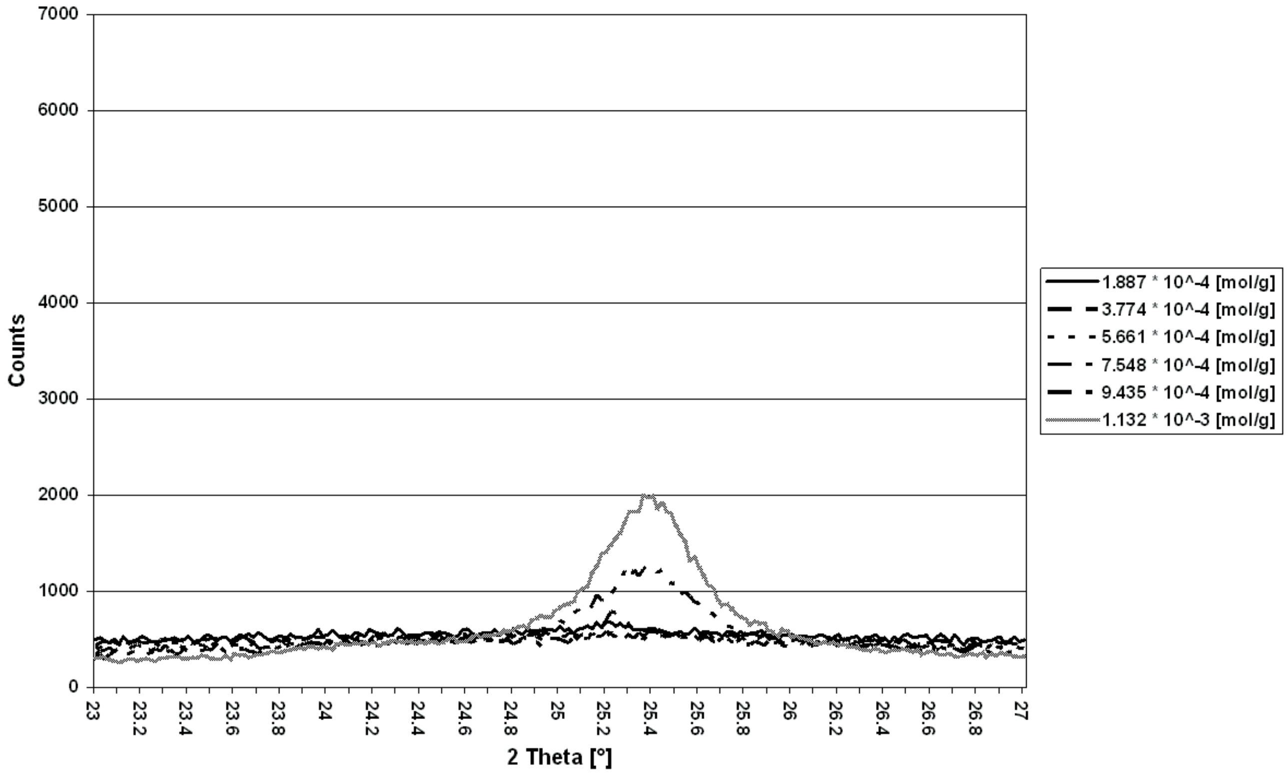

Fig. 10 XRD-scan of kieselguhr type FN 1 fluxcalcined with K_2HPO_4 at different concentrations at 1000 °C for 2 h

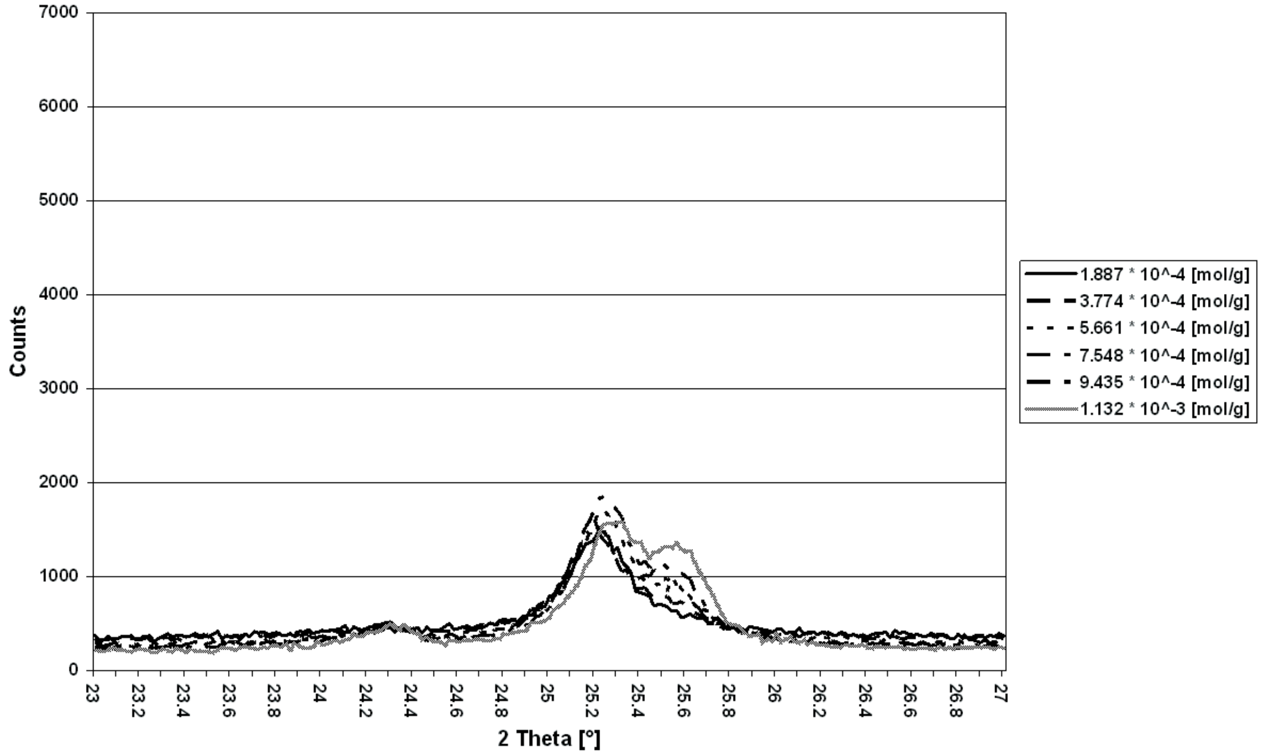

Fig. 11 XRD-scan of kieselguhr type FN 1 fluxcalcined with $CaCO_3$ at different concentrations at 1000 °C for 2 h

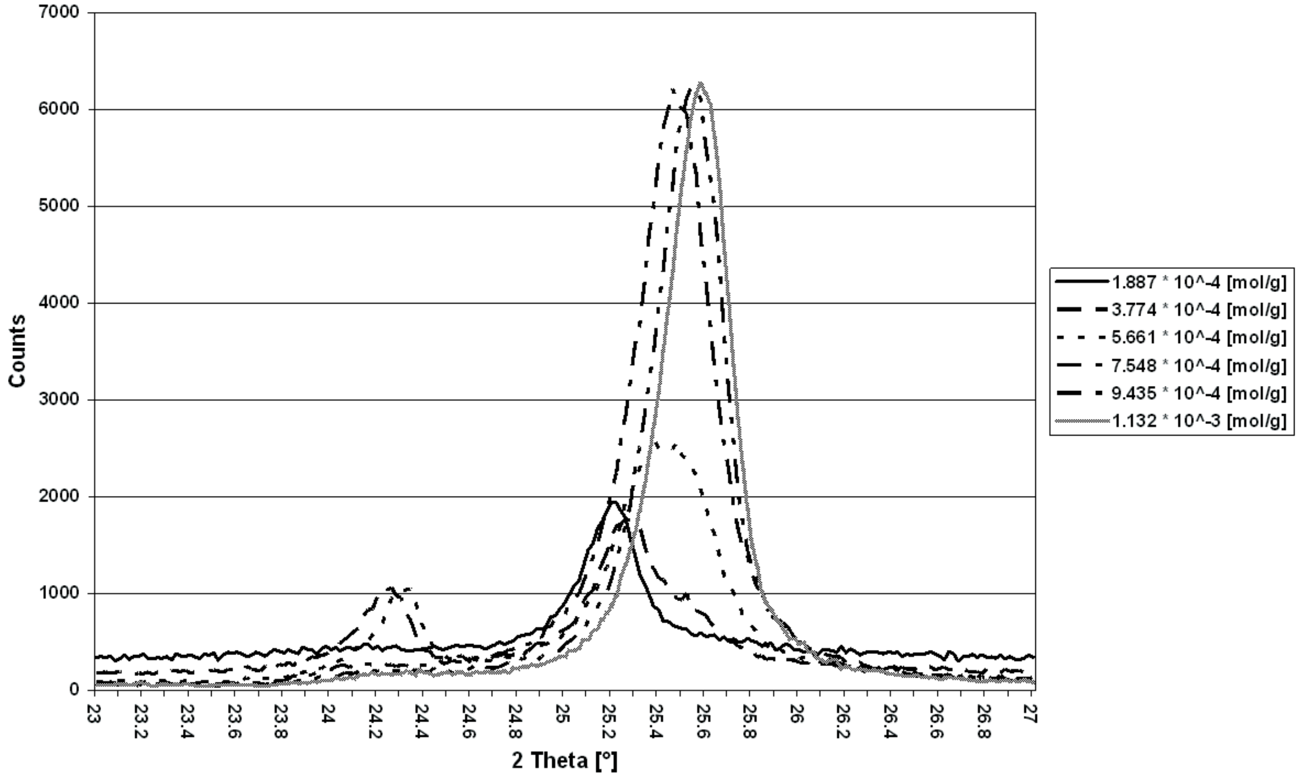

Fig. 12 XRD-scan of kieselguhr type FN 1 fluxcalcined with $CaCl_2$ x 2 H_2O at different concentrations at 1000 °C for 2 h

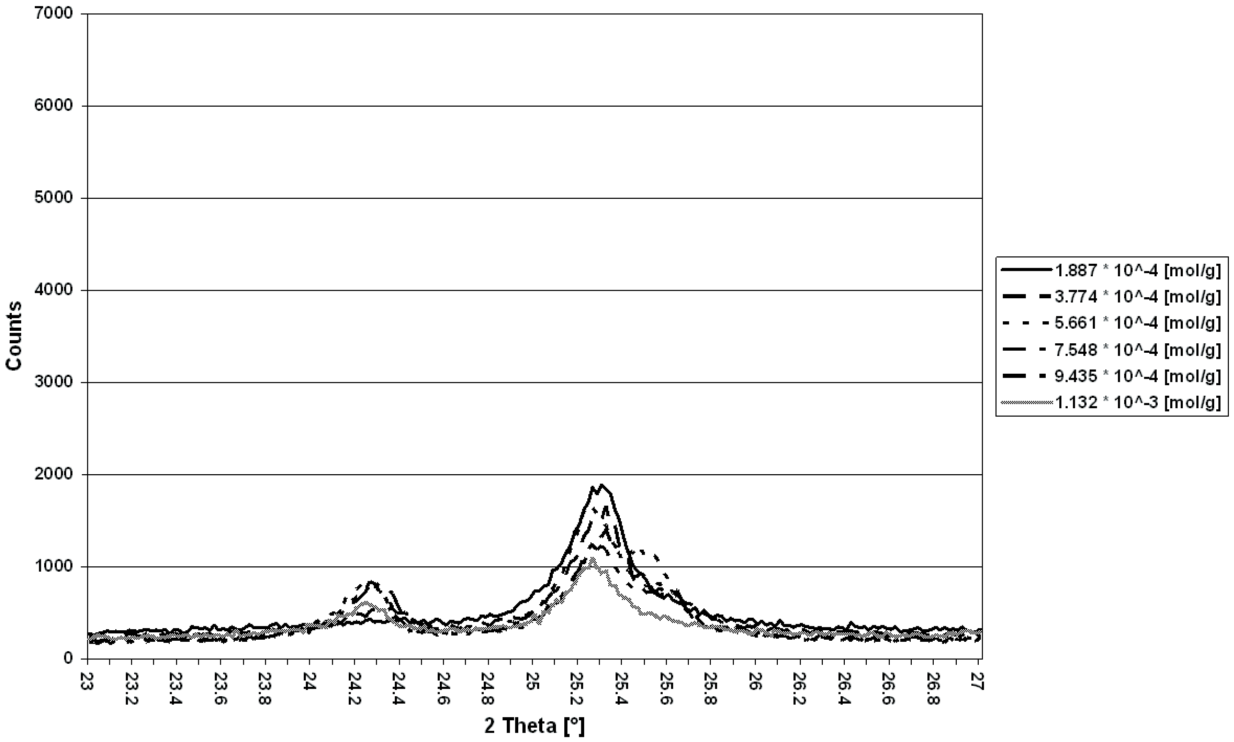

Fig. 13 XRD-scan of kieselguhr type FN 1 fluxcalcined with CaO at different concentrations at 1000 °C for 2 h

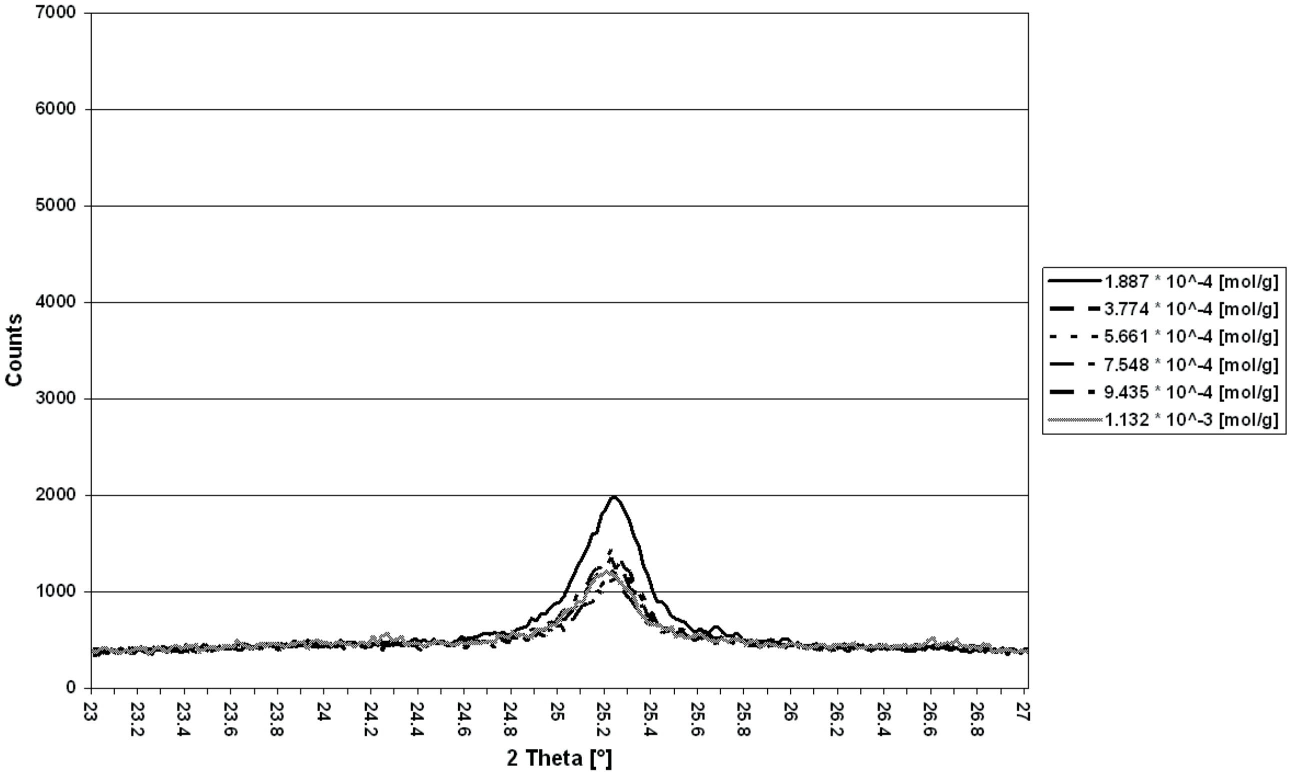

Fig. 14 XRD-scan of kieselguhr type FN 1 fluxcalcined with $MgCl_2$ x 2 H_2O at different concentrations at 1000 °C for 2 h

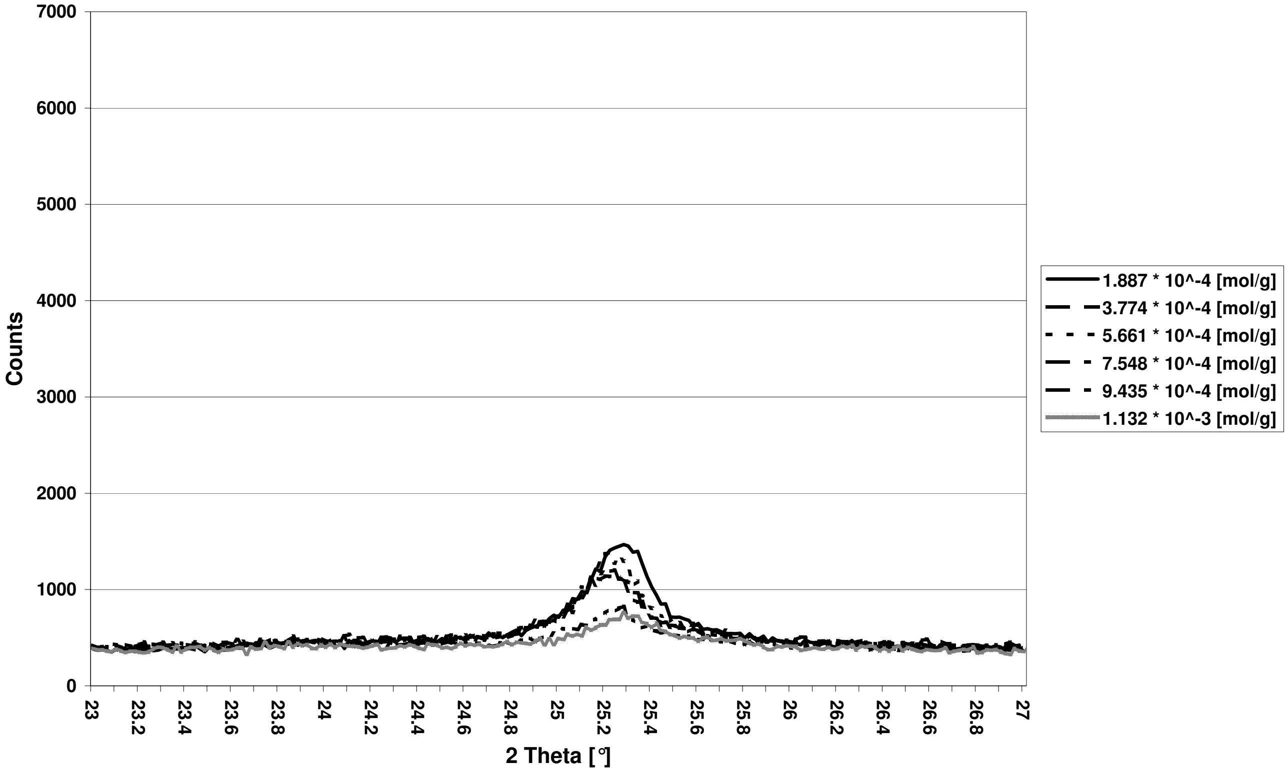

Fig. 15 XRD-scan of kieselguhr type FN 1 fluxcalcined with MgO at different concentrations at 1000 °C for 2 h