Potential of Calcined Recycling Kaolin from Silica Sand Processing as Supplementary Cementitious Material

Matthias Maier, Benjamin Forster, Nancy Beuntner and Karl-Christian Thienel

Abstract Suitability of calcined kaolinitic filter cake arising from the production of high-quality silica sand as SCM was tested. The investigation comprises two different grades of materials. The first one represents a cross section from one week of sand production. The other sample has been subsequently prepared by sedimentation on a laboratory scale in order to investigate the impact of lower sand content. Chemical and mineralogical compositions of both samples were determined by means of ICP-OES, XRD and FTIR. The laboratory sample yielded higher kaolinite and a lower quartz content in comparison with the industrial product. The dehydroxylation behavior was determined using TG/DTG. After thermal activation, the reactivity was investigated by measuring the solubility of Al- and Si-ions in alkaline solution. It turned out that a calcination temperature of at least 650 °C is required for a complete dehydroxylation. Heat of hydration was studied by isothermal calorimetry using a substitution of 20 wt% of cement by the calcined product. The same substitution was chosen for the determination of strength activity index on mortar bars. Both materials provided a significant acceleration of the early hydration by promoting the aluminate reaction. After 28 days, the higher kaolinite content of the laboratory sample leads to a higher activity index of 121% in comparison with 102% of the industrial product.

Keywords Metakaolin · SCM · Calcined clay · Recycling kaolin

1 Introduction

The high pozzolanic reactivity of metakaolin has been the subject of many studies [1]. A wide use is yet impeded by the high price, caused by the costly purification process and the high demand by competing industries like ceramic or paper industry. This reason shifted the focus of research on naturally occurring kaolinite-bearing clay as a raw material for pozzolanic cement substitutes [2]. Beyond that, clay minerals

M. Maier (✉) · N. Beuntner · K.-C. Thienel
University of the Bundeswehr Munich, Werner-Heißenberg-Weg 39, 85577 Neubiberg, Germany
e-mail: matthias.maier@unibw.de

B. Forster
Strobel Quarzsand GmbH, Freihungsand 3, 92271 Freihung, Germany

also exist as minor components in many sand or gravel deposits. During the raw material processing, which often includes a washing process, the clay-bearing fine fractions are separated as a water–solid mixture and end up as backfill in most cases. In Central Europe, 50 million tons of mineral washing sludge are produced every year [3]. Only a small percentage of it is used as raw material by the ceramic industry (e.g., less than 100,000 t per year in Germany [4]). The material investigated in the course of this study represents a residue from the washing process of a kaolin-bearing Jurassic silica sand, which is dewatered after the separation. The produced filter cake is partly used as supplementary clay for the production of clay bricks but its application is limited. This study covers first calcination trials based on a comprehensive raw material characterization, complemented by reactivity tests for an application as a supplementary cementitious material.

2   Materials and Methods

The investigated material is a fine-grained, secondary component of a siliceous sandstone, which is located in the Upper Palatinate (Bavaria, Germany) and has been exposed in several open-pit mines (Fig. 1). The outcropping sandstones exhibit a thickness of up to 30 m and are of white color, due to low iron contents. Locally, higher iron contents cause yellow, brown and red colors. The sediments belong to the geological formation of the dogger sandstone [5] with an age of approximately 171 million years [6]. Figure 1 shows on the left the sequence of the various quartz sand layers. The uppermost layer consists of brownish-colored limonite sand. Pink-colored so-called flamingo sands follow these on the bottom. The lowest layers are defined as glass sand or glass sand equivalent. These layers are characterized by their white color and high proportion of finest grain sizes (0–0.180 mm).

After transportation to the plant, the extracted sand is cleaned from interfering sediments, such as kaolinitic clays and iron and titanium-bearing minerals, in a multistage cleaning and classifying process (Fig. 2). The water required for the process is recycled in an in-house water treatment during which the washed-out

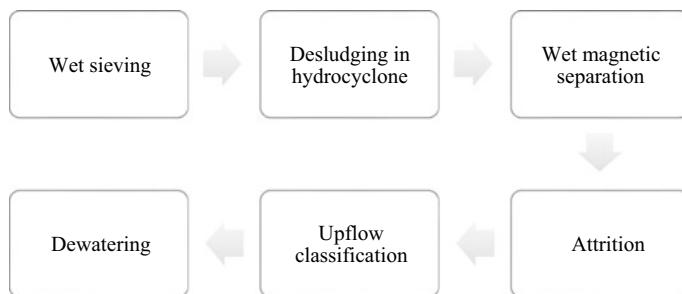**Fig. 1** Sequence of sand layers (left) and aerial view of the mining area (right)

Fig. 2 Processing scheme of the quartz sands

residual substances are separated. In the course of this process, the finest sand fraction is separated from the process water in a sedimentation cone and returned to the treatment process. The clay minerals are coagulated in the washing water by adding flocculants (anionic polyacrylamide). The settling and thickening of these flocked fine fractions are performed in the two circular thickeners. The settled fine clay gets pumped out and dewatered on chamber filter presses to a residual moisture content of approx. 20 wt%. The filter cake obtained in this process is the subject of investigation in this study.

Two grades of raw materials were investigated. The first one represented a cross section of one week of production. The second one was prepared by sedimentation on a laboratory scale. For this purpose, 1 m^3 of the sludge was removed from the storage tank of the filter press and diluted to a solid concentration of 20 wt%. Separation was executed using an 80 mm hydrocyclone test rig. The de-sanded material in the overflow of the hydrocyclone was collected in a tank together with the process water and precipitated using flocculants. The separated fine quartz was discharged via the underflow of the hydrocyclone. After a resting period of 24 h, the excess water was removed and the remaining material was dried at 105 °C in a drying cabinet.

The chemical composition of both grades of clay was measured by means of ICP-OES and is shown in Table 1. The mineralogical composition was determined by XRD (PANalytical Empyrean, Bragg-BrentanoHD monochromator, PIXcel1D linear detector) on sideloaded powder mounts to reduce preferred orientation effects, which are pronounced in well crystalline kaolinite-bearing samples. The quantitative phase composition was calculated by Rietveld refinement using Profex BGMN [7], complemented by the external standard method [8] in order to consider poorly crystalline and amorphous components after calcination. Kaolinite degree of order was analyzed from FTIR spectra of powder samples (ThermoFisher Scientific Nicolet iS10) according to Bich et al. [9] and by using models of ordered and disordered kaolinite for Rietveld refinement [10]. Calcination temperature was derived from dehydroxylation behavior, which was analyzed by means of TG/DTG (Netzsch STA 449 F3 Jupiter). For the thermal treatment, the samples were placed in platinum crucibles and calcined for 30 min in a laboratory muffle furnace. After calcination, the materials were ground in a vibratory disk mill with a speed of 700 min^{-1} for 10 min,

Table 1 Chemical composition of the raw materials

Constituent (wt%)	Industrial grade	Laboratory grade	Cement[a]
SiO_2	67.1	57.3	20.7
Al_2O_3	19.8	26.2	4.9
Fe_2O_3	5.4	6.7	2.9
CaO	0.1	0.1	65.3
MgO	0.1	0.1	1.5
MnO	n.d	n.d	0.1
TiO_2	0.9	1.1	0.3
K_2O	0.3	0.3	0.7
Na_2O	<0.1	<0.1	0.1
SO_3	<0.1	<0.1	2.9
Cl	n.d	n.d	0.1
LOI	6.3	8.2	2.3

[a]Provided by supplier

using an agate grinding tool. The calcination process was verified using FTIR and XRD. Solubility of Al- and Si-ions was measured by ICP-OES (Varian ICP-OES 720 ES) after elution of the samples for 20 h in 10% NaOH solution [11]. Heat of hydration was measured using a TAM air isothermal calorimeter at 25 °C for 48 h. For the determination of the activity index on mortar bars according to DIN EN 196–1 and for calorimetry, a CEM I 42.5 N with the chemical composition given in Table 1 was used with a substitution rate of 20 wt% and a water–solid ratio of 0.5.

3 Results

3.1 Dehydroxilation Behavior

The mass loss at approximately 280 °C (Fig. 3) could be attributed to the decomposition of iron hydroxide (e.g., Goethite). Dehydroxylation of kaolinite starts with onset between 430 and 435 °C for both samples. The reaction is accompanied by a loss of mass due to the elimination of the crystal water, which is 5.6 wt% for the industrial sample and 8.0 wt% for the laboratory sample, indicating a higher content of kaolinite for the latter.

After calcination at 550 °C, Al–OH stretching bands (Fig. 4), which indicate an incomplete dehydroxylation, are still visible. After 650 °C, Al–OH bands are no longer present.
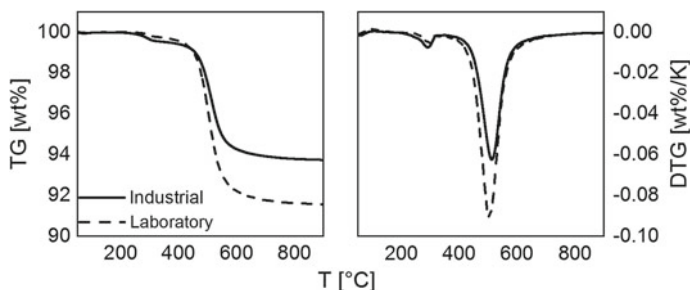
Fig. 3 Thermogravimetric analysis of the two different grades
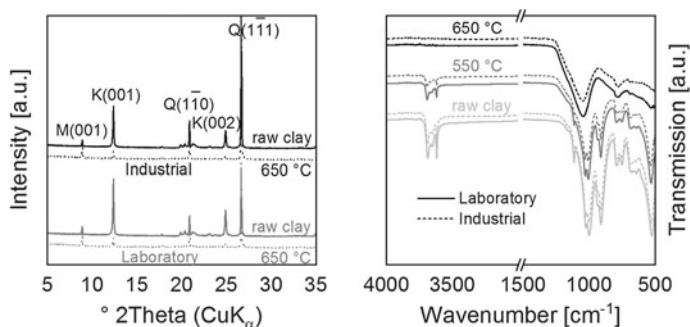

Fig. 4 X-ray diffractogram (left) and FTIR spectra (right) of the two different grades in dependence of calcination temperature (M = Muscovite, K = Kaolinite, Q = Quartz)

3.2 Mineralogical Properties

The secondary hydrocyclone reduced the quartz content from 47.3 to 29.3 wt%, while increasing the kaolinite content from 44.5 to 62.3 wt%. The complete mineralogical composition before and after calcination is given in Fig. 5 (left). Based on the ratios of the Al–OH bands in the FTIR spectra in the range between 3600 and 3700 cm^{-1}, the degree of order of the kaolinite was determined by calculating the indexes P0 (0.97) and P2 (1.02), which implicate an intermediate degree of order according to Bich et al. [8]. The results from Rietveld refinement reveal a mixture of ideally ordered and stacking disordered kaolinite (Fig. 5, right).

While the FTIR spectra indicate a complete dehydroxylation at 650 °C, the diffraction patterns still show small kaolinite reflexes which can be quantified to 6.9 wt% for the industrial and 7.7 wt% for the laboratory sample. Since no more OH vibrations can be detected, these reflexes may also represent relics of a dehydrated kaolinite lattice, which did not break down completely during calcination.
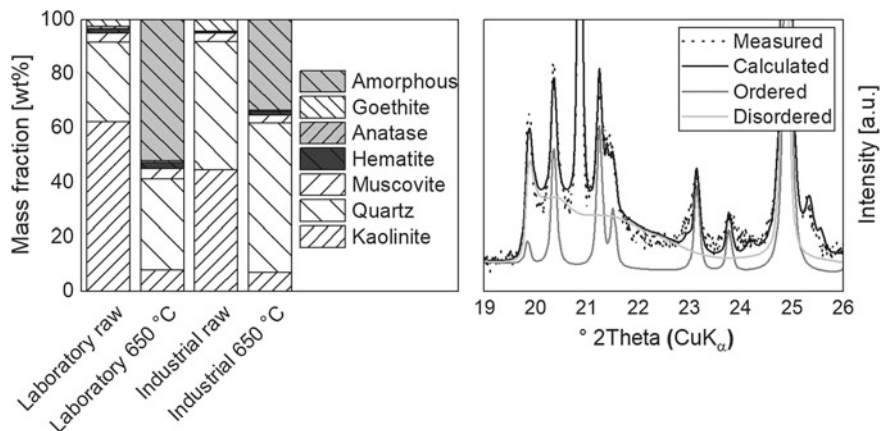
Fig. 5 Quantitative phase composition of two different samples before and after calcination (left) and refinement of structure models of ordered and stacking disordered kaolinite (right)

3.3 Reactivity

Solubility of Al- and Si-Ions

The pozzolanic reactivity of calcined clay depends to a large extent on the amount and proportion of soluble aluminum and silicon ions in alkaline solution. The solubilities are shown in Fig. 6 for both samples and both calcination temperatures. The bars show the total solubility of Al- and Si-ions in mmol/l. The numbers above the bars indicate the Si–Al ratio and are close to 1 for all samples, which is typical for metakaolin. As already seen from the FTIR spectra, almost complete dehydroxylation of the kaolinite is only ensured at a temperature of at least 650 °C, which is reflected in an Al and Si solubility being more than twice as high compared to 550 °C. The laboratory sample exhibits a solubility of Al- and Si-ions that is about 50% higher

Fig. 6 Solubility of Al- and Si-ions after elution in 10% NaOH solution for 20 h
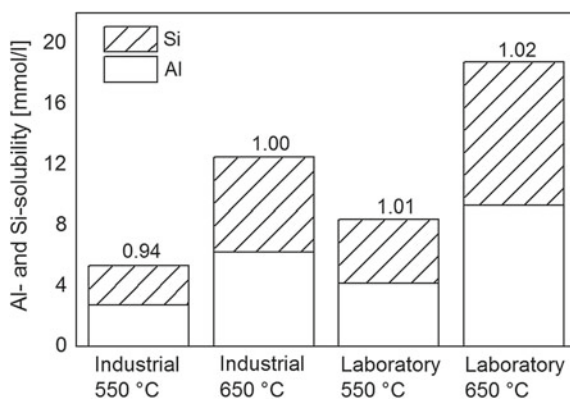
than that of the industrial sample for both calcination temperatures. Due to these results, calorimetric and strength measurements were only conducted for the 650 °C samples.

Heat of Hydration

Within the first hours, both substituted samples have a similar course of heat flow as the reference (Fig. 7), whereby the samples with calcined clay show a slightly higher heat flow in the dormant period and a slightly faster acceleration period relative to the cement content. In the reference sample, the aluminate reaction is recognizable as a clear shoulder of the silicate heat peak. The influence of the calcined clays can be seen in the acceleration and amplification of the aluminate reaction, which leads to a superposition of the two reactions for the laboratory sample. The heat of hydration after 48 h is 236 J/g_{cement} for the reference, 252 J/g_{cement} for the substitution with 20 wt% industrial grade and 269 J/g_{cement} for the substitution with 20 wt% laboratory grade. From this, a clear contribution of both calcined materials to the early hydration can be derived.

Activity Index

The development of compressive strength related to the reference is shown in Fig. 8. After two days, a significant strength contribution was detected for both samples. This contribution slows down until 7 days but is still present as the activity index exceeds 80% for both systems. After 28 days, the compressive strength of the mortar substituted with the industrial grade sample corresponds approximately to that of the reference while the mortar substituted with the laboratory grade sample reaches an activity index of 121% of the reference strength.
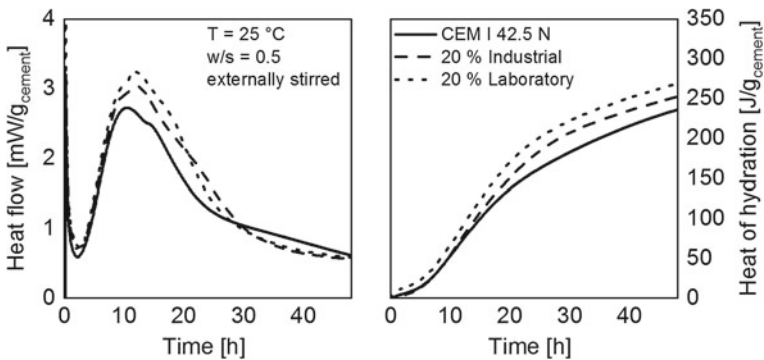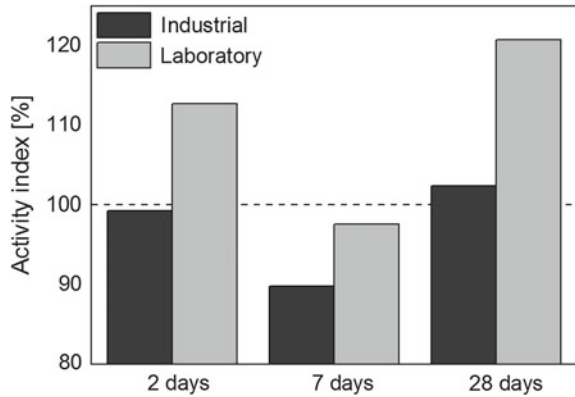

Fig. 7 Comparison of heat flow and cumulative heat during the first 48 h of hydration

Fig. 8 Comparison of activity indexes after 2, 7 and 28 days

4 Conclusion

Both investigated samples show a high potential regarding the use as SCM. The pozzolanic reactivity indicated by the high solubilities of Al- and Si-ions could be confirmed by a significant contribution to the early hydration and the strength activity indexes within the first 28 days. As expected, the laboratory grade material provides a higher reactivity due to a higher proportion of kaolinite, reached by the supplementary sedimentation process. While a calcination temperature of 550 °C is not yet sufficient, an almost complete conversion from kaolinite to metakaolin takes place at 650 °C. For further studies, the temperature will be raised to 680 °C to ensure complete dehydroxylation. Nevertheless, the activation temperature is still in a very interesting range from an ecological and economical point of view. This study confirms that clay-bearing mineral residues can provide a high potential as resource-efficient raw materials for the production of SCM and should get high attention in the search for appropriate materials.

References

1. Sabir, B.B., Wild, S., Bai, J.: Metakaolin and calcined clays as pozzolans for concrete: a review. Cem. Concr. Compos. **23**(6), 441–454 (2001)
2. Scrivener, K., Martirena, F., Bishnoi, S., Maity, S.: Calcined clay limestone cements (LC3). Cem. Concr. Res. **114**, 49–56 (2018)
3. Schmitz, M., Röhling, S., Dohrmann, R.: Waschschlamm: Ein vernachlässigtes heimisches Rohstoffpotenzial? Gesteinsperspektiven **8**, 16–18 (2011)
4. Krakow, L.: Resource efficiency in the clay brick and roofing tile industry Part I: general introduction. ZI Ziegelindustrie International **01–02**(12), 15–24 (2012)
5. Börner, A.: Steine- und Erden-Rohstoffe in der Bundesrepublik Deutschland, 1st edn. E. Schweizerbart'sche Verlagsbuchhandlung, Hannover (2012)
6. Elsner, H.: Kaolin in Deutschland. Federal Institute for Geosciences and Natural Resources, Hannover (2017)

7. Döbelin, N., Kleeberg, R.: Profex: a graphical user interface for the Rietveld refinement program BGMN. J. Appl. Crystallogr. **48**, 1573–1580 (2015)
8. O'Connor, B.H., Raven, M.D.: Application of the Rietveld refinement procedure in assaying powdered mixtures. Powder Diffr. **3**, 2–6 (1988)
9. Bich, C., Ambroise, J., Péra, J.: Influence of degree of dehydroxylation on the pozzolanic activity of metakaolin. Appl. Clay. Sci. **44**(3–4), 194–200 (2009)
10. Ufer, K., Kleeberg, R., Monecke, T.: Quantification of stacking disordered Si-Al layer silicates by the Rietveld method: application to exploration for high-sulphidation epithermal gold deposits. Powder Diffr. **30**(S1), 1–8 (2015)
11. Buchwald, A., Kriegel, R., Kaps, C., Zellmann, H.-D.: Untersuchung zur Reaktivität von Metakaolinen für die Verwendung in Bindemittelsystemen. In: 7th Gesellschaft Deutscher Chemiker e.V –Jahrestagung, München (2003)