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The Influence of Production Parameters on Pozzolanic Reactivity of Calcined Clays



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ABSTRACT

Calcined clays are gaining increasing interest as future supplementary cementitious materials for the production of blended cements. Besides the mineralogy, the right production conditions can affect the pozzolanic activity of calcined clays. In this paper, the pozzolanic reactivity of two calcined natural clays in dependence of burning temperature, residence time in the furnace, cooling conditions and particle size of the final product is investigated. The highest pozzolanic reactivity was found at calcination temperatures between 600 and 800°C. While different cooling conditions had no identified effect on reactivity, decreased particle size and residence time increased the reactivity.

Key words: Calcined clay, pozzolana, lime consumption, heating, particle size.

1. INTRODUCTION

Portland cement is the key binder for concrete production. However, cement production is a highly energy intensive process which emits around 900 kg CO₂ for every ton clinker produced [1]. The cement industry was identified to be the amongst the largest carbon dioxide emitters with about 5-7% of the total global CO₂ emissions [2]. About 60% of the CO₂ emissions derive from the decomposition of limestone during firing. The remaining 40% are combustion related emissions like the use of fossil fuels as well as the energy requirement during processes like drying and grinding [3]. Possible measures to reduce these CO₂ emissions are (1) improvement of energy efficiency of cement plants; (2) utilization of alternative fuels; (3) carbon dioxide capture and (4) producing blended cements with less clinker content [4-6]. In the short term, the most promising approach to lower CO₂ emissions from the cement industry is the production of blended cements. i.e. replacing increasing amounts of cement clinker with supplementary cementitious materials e.g. calcined clays [7]. Reducing the amount of cement clinker by e.g. calcined clays in binders, directly reduces the CO₂ emissions associated with clinker productions. Additionally, the production of calcined clays happens at lower temperatures compared to cement and less energy is required for grinding calcined clay lumps.

The most commonly used supplementary cementitious materials (SCMs) in the cement industry today are granulated blast furnace slag (GBFS) from the steel industry and fly ash from coal power plants. These SCMs proved suitable to reduce the clinker content while maintaining or enhancing the properties of the final product. However, the availability of these materials is potentially getting limited and cannot meet the future demand of the large cement industry on a sustained basis. As these materials derive from processes associated with CO₂ emissions themselves, their supply may drop in the long-run when coal fired power plants and blast furnace plants are replaced by less CO₂ intensive processes [6, 8]. Consequently, for the long term the right choice of the replacing material is mainly a question of availability [9].

Natural pozzolanic materials like clays are a promising alternative SCMs as they are abundant and widespread with huge deposits distributed all over the world. Mining and transportation costs would be rather low so that these materials have the potential to serve the cement industry sufficiently for a sustainable future. Still, clays are very complex materials regarding the chemical and mineralogical composition. It is well known, that the right calcination temperature to produce reactive calcined clays depends a lot on the clay mineralogy [10-14]. Depending on the mineral composition, calcination at temperatures usually between 600 and 800°C, leads to the formation of an active metastable state with high pozzolanic activity [10, 11]. Kaolinite clays show higher pozzolanic reactivity than smectite or illite clays. The clays presented in this study have been investigated by the present authors in earlier studies. It was shown that replacement of up to 50% cement by calcined clay can result in equal or higher 28 day compressive strength [10, 15-19].

Besides the mineralogy and calcination temperature, other parameters during production potentially influence the reactivity of the final product. In addition to calcination temperature, this paper focuses on the effect of cooling rate, residence time in the furnace and particle size after milling, on the pozzolanic reactivity of two natural calcined clays. The understanding of the effect of these parameters can contribute to optimisation of potential industrial scale production of calcined clays.

2. MATERIALS AND METHODS

2.1 Materials

Tables 1 and 2 show the bulk mineralogy of crystalline phases and the chemical composition of the two investigated clays. In earlier work on the pozzolanic activity of 7 different clays, Clay A and Clay B showed highest reactivity [10] and were therefore chosen for further investigations on the impact of production parameters. The main mineral phases of Clay A are kaolinite, quartz and feldspar. Clay B is a smectite rich clay with about 25% calcite. Calcined Clay B has been extensively studied by the present authors and was published under the name “calcined marl” for simplicity [15-19]. However, it should actually be categorized as “calcareous mudstone”. Clay B is a tertiary sediment and was deposited between the middle and late Eocene (56 to 33.9 million years ago) in a marine depositional environment [20]. The calcite content derives to a large portion from coccoliths.

Calcium hydroxide ($\text{Ca}(\text{OH})_2$) used in lime consumption tests was laboratory grade from Merck company.

Table 1 - Mineralogical composition of the raw clays in weight%.

| Phase | A (%) | B (%) |
|-------------------|-------|-------|
| Kaolinite | 46.7 | 8.4 |
| Smectite | — | 53.5 |
| Illite | — | 4.4 |
| Muscovite | 1.5 | — |
| Quartz | 17.5 | 4.3 |
| K-feldspar | 34.3 | — |
| Calcite | — | 24.7 |
| Siderite | — | 3.1 |
| Pyrite | — | 1.3 |

Table 2 - Chemical composition of the investigated clays in weight%.

| Oxide | A (%) | B (%) |
|------------------------------------|-------|-------|
| SiO₂ | 60.6 | 48.7 |
| Al₂O₃ | 30.0 | 17.8 |
| Fe₂O₃ | 3.4 | 10.4 |
| CaO | 0.1 | 13.8 |
| K₂O | 3.2 | 2.4 |
| Na₂O | — | 0.7 |
| MgO | 0.4 | 2.8 |
| MnO | 0.0 | 0.2 |
| P₂O₅ | 0.10 | 0.2 |
| TiO₂ | 0.4 | 1.0 |

2.2 Methods

A detailed characterisation of the raw and calcined clays including quantitative X-Ray powder diffraction (XRPD) using the Rietveld method, infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), nuclear magnetic resonance spectroscopy (NMR) and mössbauer spectroscopy is presented in [21]. The mineralogical analysis of the raw clays (Table 1) was performed with XRD. The bulk mineralogy of Clay A and B was determined on dried and

ground samples using the back-loading technique. The $\leq 2 \mu\text{m}$ fraction (clay fraction) was separated from the bulk by sedimentation, smeared on a glass plate and dried in air. The clay fraction was then investigated under three different conditions (a-c); a: untreated, b: after treatment with ethylene glycol vapours in a desiccator for 24 h at 60°C , c: after heating at 500°C for 1 h. For analysis, a PAN Analytical X'Pert Pro MPD equipped with an X'Celerator RTMS detector, an automatic divergence slit and a Cu-K α X-ray source was used. The samples were measured from 2 to $65^\circ 2\theta$ using a step size of $0.0170^\circ 2\theta$ and a step time of 20 s. Data were collected at 45 kV and 40 mA. More details on the procedure of quantitative mineralogical analysis can be found in [22, 23].

XRPD was also used to qualitatively analyse the calcined clay samples and check possible differences in the phase assemblage in dependence of the different burning conditions. Here, XRPD measurements were done with a D8 Focus from Bruker, equipped with a Cu K α X-Ray source and Lynx Eye detector. Data were collected with a step size of $0.2^\circ 2\theta$ and a time of 1 s per step.

The chemical composition (Table 2) of the investigated clays was measured with X-Ray fluorescence (XRF) using a Bruker AXS S8 Tiger WDXRF instrument. Dried and powdered clay samples were ignited at 850°C . Then 0.5 g of the dried clay sample was added to 5.0 g of a 2:1 mix of lithium- tetraborate and metaborate and 60 μg of lithium iodide. The mixture was fused in a Pt crucible and moulded to a glass disk.

Samples of about 15 g raw Clay A or Clay B were burned at different temperatures in a laboratory electrical furnace. Raw clay was weight in a platinum crucibles and placed in a chamber furnace from Nabertherm (Model: LH 60/14) at temperatures between 400 and 1100°C . The clays were placed directly into the furnace at the desired burning temperature.

To test the effect of cooling rate on the pozzolanic reactivity, the clays were hold for 2 h at constant temperature. After heating, one sample was taken out of the furnace and quenched in air for immediate cooling. A second sample was left in the furnace to cool down slowly to room temperature overnight.

To test the effect of particle size on the pozzolanic reactivity, half the amount of the clays, burned under the same conditions as mentioned above, was milled down to $<50 \mu\text{m}$. The remaining amount was milled down to particle sizes $<10 \mu\text{m}$. Milling of the calcined samples was done by hand using an agate mortar. The clay powder was milled and sieved until the desired particle size was reached. Only particles passing the sieve with a 50 and 10 μm mesh size respectively, were used for the tests.

To test the effect of heating rate on the pozzolanic activity, an additional set of samples was hold in the furnace for 30 min at a given temperature. The samples burned for 30 min were cooled down rapidly as described above and milled down to $<10 \mu\text{m}$.

To investigate the pozzolanic activity of the calcined clays, pastes of calcined clay and calcium hydroxide ($\text{Ca}(\text{OH})_2$) were mixed. From here, the term lime will be used for $\text{Ca}(\text{OH})_2$. Pastes were mixed in a calcined clay/lime ratio of 1/1 and a water to binder ratio of about 0.9. To simulate pore solution of cement pastes an alkaline solution of pH 13.2 and a KOH/NaOH ratio of 2/1 was used as mixing water. The pastes were mixed by hand during 60 s and transferred into glass bottles. The sealed glass bottles were cured during 28 days at 20°C . After 28 day curing the hydration was stopped by solvent exchange. Pastes were crushed and washed with

ethanol several times. The filtrated powder was dried in a closed desiccator at 35% RH upon saturated CaCl_2 solution. The amount of lime left in the pastes after 28 days was measured with thermogravimetric analysis (TG). The lime consumption gives a direct correlation to the pozzolanic activity of the calcined clays.

TG analysis was performed with a Mettler Toledo TGA/SDTA 851. First, samples were dried at 40°C for two hours in the TG apparatus. In a second step, the samples were heated from 40 to 1100°C with a heating rate of $10^\circ\text{C}/\text{min}$. The purge gas was in both steps nitrogen (N_2) with a flow of 30 ml/min. The decomposition of $\text{Ca}(\text{OH})_2$ takes place between 450 and 550°C and shows in a clear weight loss. By measuring this weight loss the remaining $\text{Ca}(\text{OH})_2$ content after 28 days relative to the content in the initial mixture was calculated. The exact boundaries for the temperature interval of $\text{Ca}(\text{OH})_2$ were read from the 1st derivative curve of thermogravimetric analysis (DTG). The weight loss calculated from the difference of the horizontal tangents in the TG signal was multiplied with the molar ratio $74/18$ for $\text{Ca}(\text{OH})_2$ and H_2O , respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of cooling rate on the pozzolanic activity

Figure 1 and 2 show the XRD diffractograms of Clay A and Clay B calcined between 400 and 1100°C . In both cases the clays were hold for 2 h in the furnace at a given temperature and then taken out from the furnace and quenched in air, i.e. fast cooling. In case of Clay A there was no difference detectable in the crystalline phase assemblage between the fast and slow cooled samples. Kaolinite disappeared above 600°C . This might be due to dehydroxylation of the clay mineral structure and transformation to metakaolin [11]. Muscovite peaks are visible up to 1000°C . Feldspar and quartz were not affected by the heat treatment up to 1000°C . At 1100°C recrystallization of mullite was observed. Recrystallization of other high temperature phases was not observed.

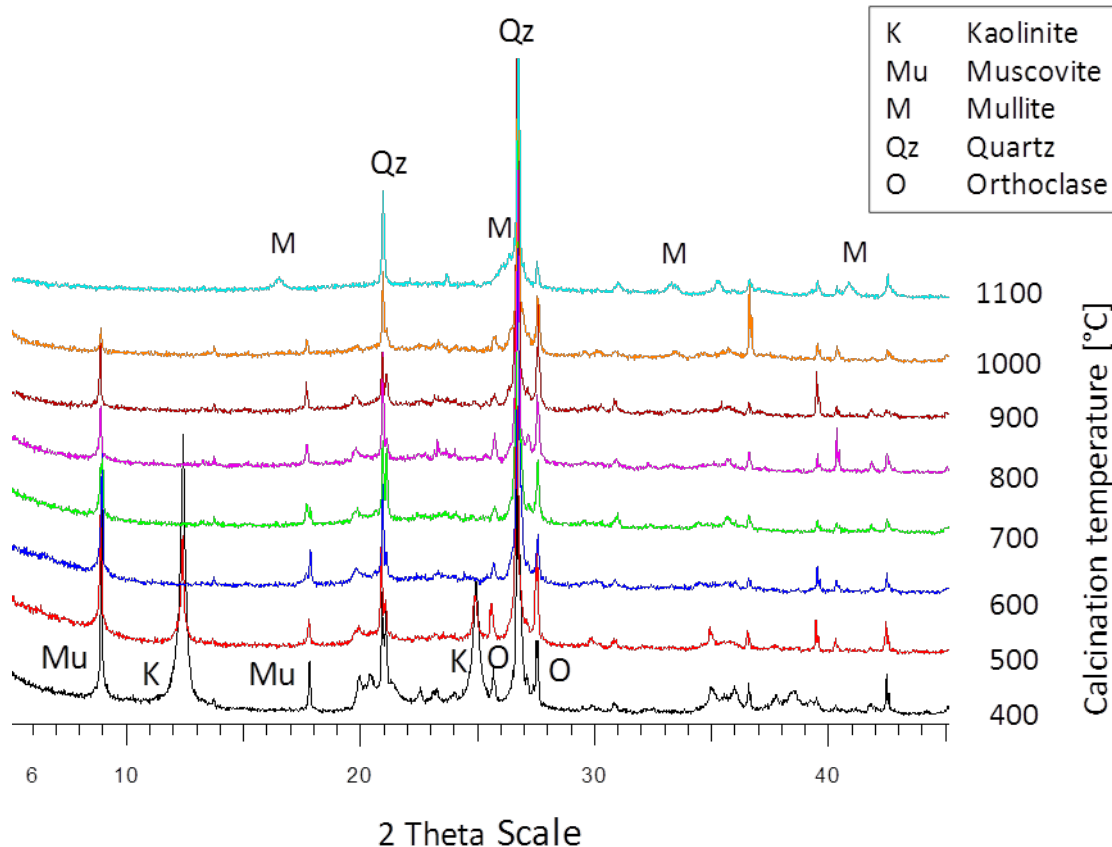


Figure 1 - XRD diffractograms of Clay A burned between 400 and 1100°C with fast cooling.

In case of Clay B, minor differences were observed in the phase assemblage of the fast and slow cooled samples. At 800°C calcite was completely decomposed in both samples. The main calcite peak at 29.4° 2Theta was visible until 700°C. The smectite peak at about 9° 2Theta steadily decreased from 400 to 800°C and completely disappeared at 900°C. It can be seen that the smectite peak is at about the same 2Theta angle than the muscovite peak in Clay A. Originally, non dried smectite shows a main peak at about 6° 2Theta. However, due to drying and the loss of interlayer water the distance between the different layers in the smectite structure decreases, causing a peak shift to higher 2 Theta values. Recrystallization of anorthite, diopside - wollastonite and hematite was detected between 900 and 1100°C. Gehlenite was only found as an intermediate phase at 1000°C in the fast cooled sample. Gehlenite might be a metastable phase transforming to more stable phases like anorthite when cooled down slowly [10]. The intense peaks at ~ 21 and 43° 2Theta in the sample calcined at 700°C belong to quartz (Figure 2). The high intensity in just this sample might be explained with an effect called spottiness, i.e. large quartz grains in diffraction position.

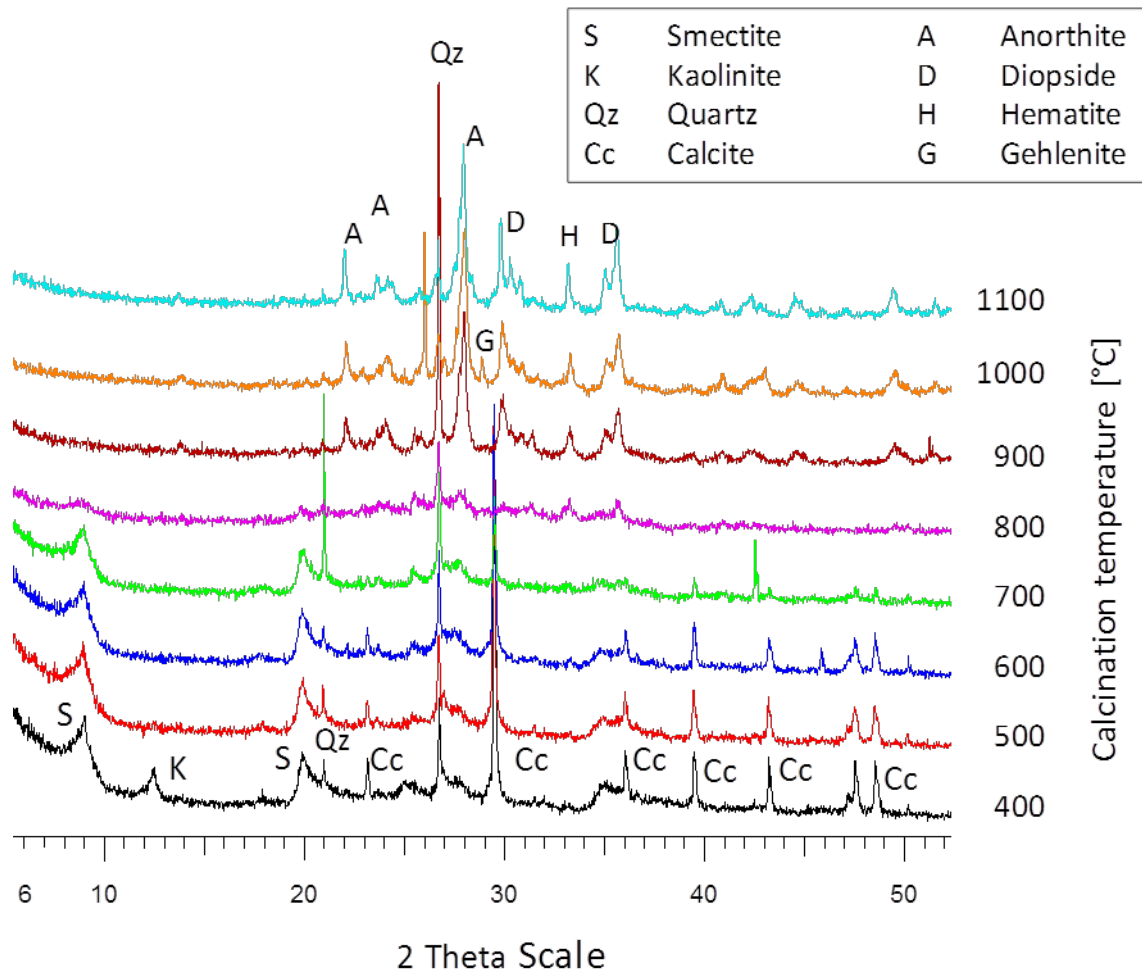


Figure 2 - XRD diffractograms of Clay B burned between 400 and 1100°C with fast cooling.

The lime consumption of fast and slowly cooled Clay A and Clay B burned between 400 and 1000°C is shown in Figure 3. Here, all clays were milled to a particle size <10 μm. The accuracy of the lime consumption values is about 5% [10]. The reactivity of both clays seemed not be affected by slow or fast cooling. Clay A showed the highest pozzolanic reactivity between 600 and 800°C with a lime consumption between 0.61 and 0.64 g lime/g clay. The low reactivity at 400 and 500°C might be due to the not yet dehydroxylated kaolinite and hence the incomplete transformation to metastable metakaolin. At a calcination temperature above 900°C the reactivity decreased as a result of starting recrystallization of new stable phases. In earlier investigations [10] it was suggested that to reach the maximum pozzolanic reactivity of Clay B, calcite should not be completely decomposed. This was confirmed in Figure 3. At 700°C, when calcite is still present to a certain amount, the pozzolanic reactivity is higher, compared to the sample calcined at 800°C. At 800°C, calcite was completely decomposed (Figure 2). The considerable drop in pozzolanic reactivity from 800 to 900°C was due to recrystallization of high temperature phases (Figure 2). It can be seen that Clay A in total has a higher pozzolanic reactivity with higher lime consumption than Clay B. This is because kaolinite clay minerals are more reactive than smectite clay minerals when calcined [11].

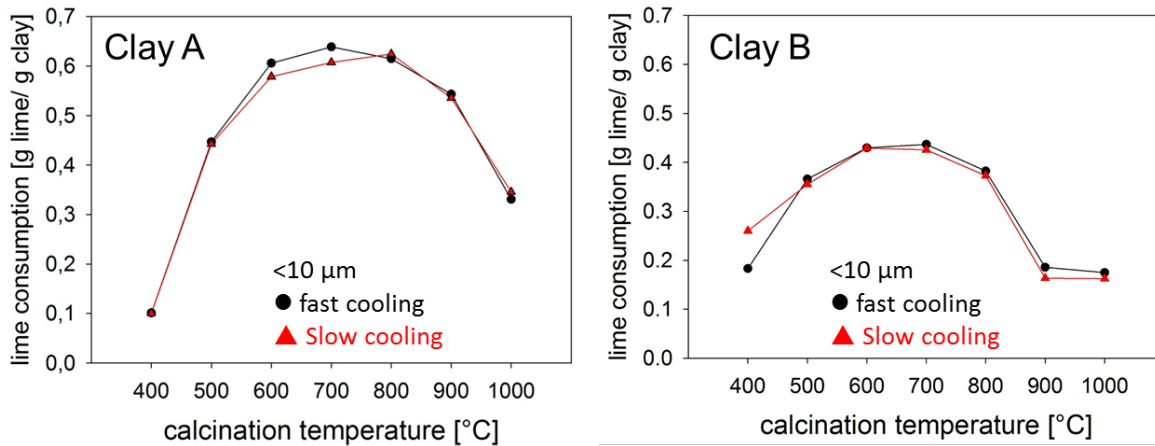


Figure 3 - Lime consumption in g lime/g clay for Clay A and Clay B burned between 400 and 1000°C with fast and slow cooling. Particle size was <10 μm.

3.2 Effect of residence time on the pozzolanic activity

Figure 4 shows the comparison of the lime consumption of Clay A and Clay B calcined for 120 min and 30 min between 400 to 1000°C. New samples were produced with shorter residence time of 30 min. The new samples were burned from 400 to 900°C in steps of 50°C. All samples were *rapidly* cooled and milled down to particle sizes <10 μm.

In case of Clay A, a shorter residence time of 30 min increased the pozzolanic reactivity by about 0.1 g lime/g clay between 550 to 650°C. It is also shown that the lime consumption was rather stable between 550 and 900°C. In earlier investigations it was shown that lime consumption of the investigated clays shows a good correlation to 28 day compressive strength of mortars with 20% replacement of cement by calcined clay [10]. A lime consumption of about 0.7 g lime/g clay of Clay A corresponded to a compressive strength increase of about 15% when 20% cement was replaced with calcined Clay A [10]. Taking this correlation into account, we can assume that Clay A can be burned in this wide temperature range with a relatively short residence time in the kiln, without changing its pozzolanic properties in cementitious systems considerably. This can be important for production, where minor temperature variations should not have a big effect on the final product.

In case of Clay B, the pozzolanic reactivity increased slightly when calcined with lower residence times of 30 min. The reactivity had a peak at 650°C and decreased continuously above that temperature. This shows that Clay B is more sensitive to temperature with a narrower window of highest reactivity.

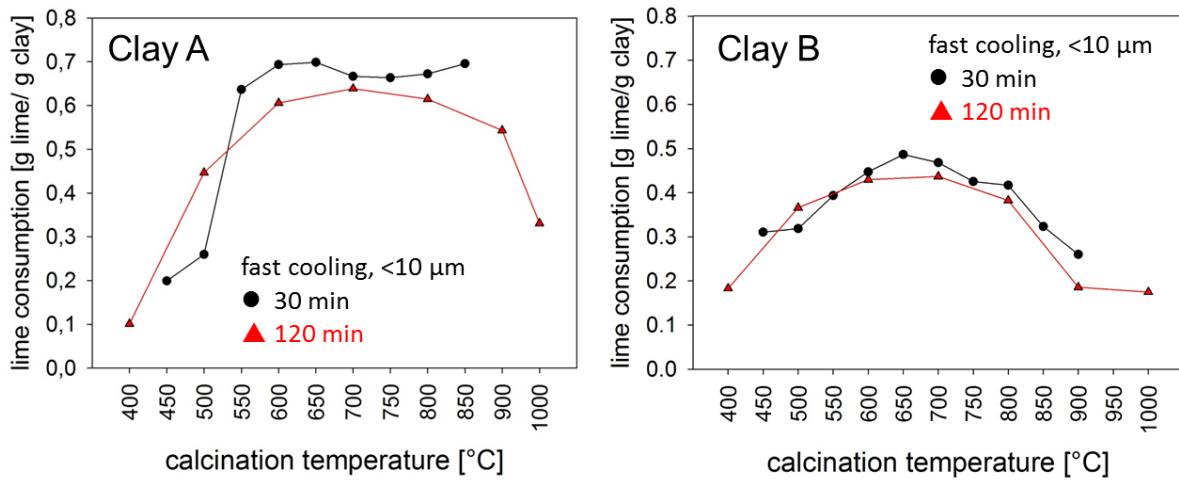


Figure 4 - Lime consumption in g lime/g clay for Clay A and Clay B burned between 400 and 1000°C with a residence time of 30 and 120 min in the furnace.

3.3 Effect of particle size on the pozzolanic activity

Figure 5 and 6 show the lime consumption of slowly and rapidly cooled Clay A and Clay B, respectively, as a function of their particle size. For both calcined clays the finer ground samples showed higher pozzolanic reactivity. In case of Clay A the lime consumption was increased by about 0.1 g lime/g clay (20% increase) when the particle size was decreased from <50 to <10 μm . For Clay B (Figure 6) the difference in lime consumption was even higher between the fine and coarse ground samples. In the Clay B samples with particle sizes <50 μm , the lime consumption was almost constant between 500 and 800°C.

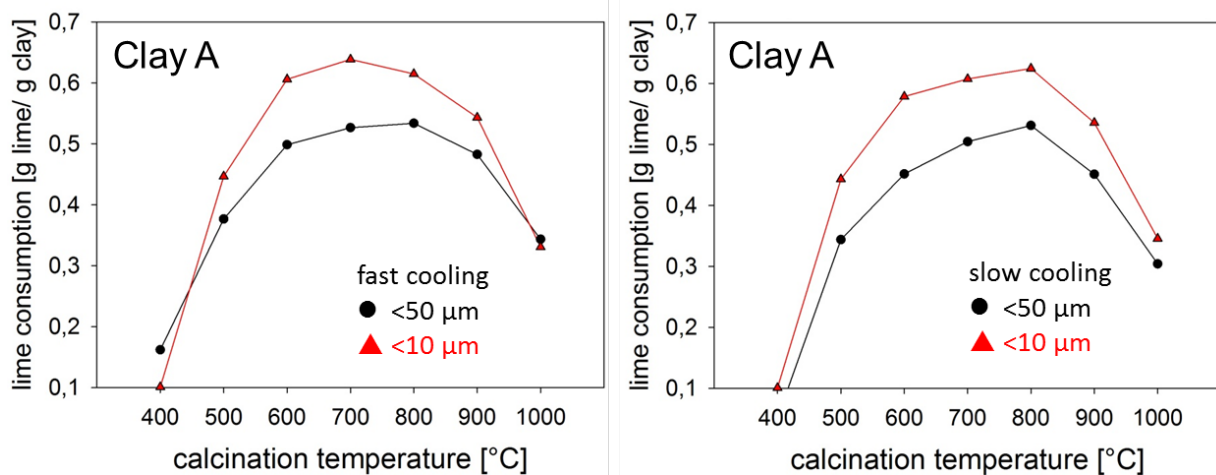


Figure 5 - Lime consumption in g lime/g clay for Clay A burned between 400 and 1000°C with fast (left) and slow cooling (right) and milled down to <50 μm and <10 μm .

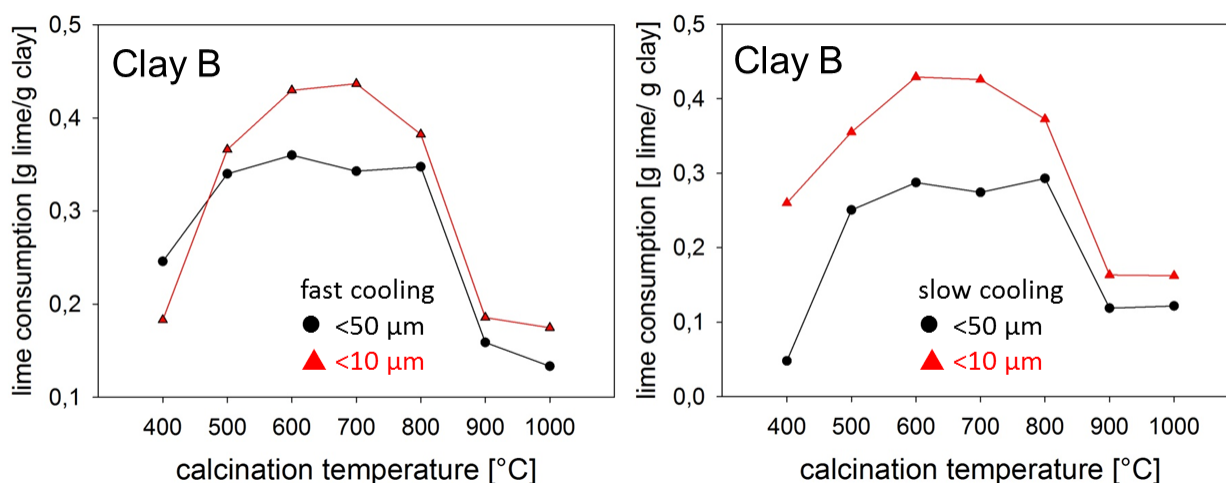


Figure 6 - Lime consumption in g lime/g clay for Clay A burned between 400 and 1000°C with fast (left) and slow cooling (right) and milled down to <50 μm and <10 μm.

4. CONCLUSIONS

In this paper, the pozzolanic reactivity of two natural calcined clays was investigated in dependence of calcination temperature, cooling rate, residence time and particle size after milling. The obtained results give valuable contributions to an optimisation of a potential industrial scale production of calcined clays. The main results are listed below:

- Both calcined clays showed highest pozzolanic reactivity between 600 and 800°C
- The kaolinite rich clay showed higher pozzolanic reactivity than the smectite rich clay.
- The cooling rate had no identified effect on the pozzolanic reactivity of the calcined clays.
- A decreased residence time from 120 to 30 minutes increased the pozzolanic reactivity.
- Particle size (<10 μm) had the strongest effect on the pozzolanic reactivity. A smaller particle size increased the pozzolanic reactivity of calcined clays.

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