

Stability of calcined clays during storage

Katja Pesch, Simone E. Schulze, Jörg Rickert, VDZ Technology gGmbH, Düsseldorf

Abstract

Usage of calcined clay as a cement main constituent is spotlighted as an important part of the decarbonisation of the cement industry. In particular, little knowledge is available on the storage stability of calcined clays. Therefore, the influences of fineness, temperature and humidity for different timescales of storing were determined.

Two samples of a calcined kaolinitic-illitic clay of different fineness (crushed and ground) were stored sealed in a desiccator, as well as at 20 °C and 60 % rel. humidity, and at 40 °C and 100 % rel. humidity. The clay's mineralogical composition, moisture and chemically bound water content were analysed at 7, 28, and 91 days of storage respectively. Additionally, their reactivity was determined acc. ASTM C 1897-20 and acc. EN197-1.

The calcined clays which were stored in a desiccator showed only slight alteration over the period of 91 days. Samples stored at 20 °C and 60 % rel. humidity, contained small amounts of moisture and chemically bound water, regardless of their fineness. Storage at 40 °C and 100 % rel. humidity led to a huge increase in moisture and chemically bound water, especially at high fineness. The reactive silicon of the fine samples was diminished independent of storage conditions over time, whereas the coarse samples showed no changes. Samples stored at 40/100 showed a strong decrease in their heat of hydration over 91 days.

This study implicates, that the analysed calcined clay could be stored as coarse-grained fraction at normal conditions.

Keywords

Calcined clays, storage, pozzolanic reactivity, aging

1 Introduction

The production of cements with calcined clay is a key element in the CO₂ reduction strategy of the cement industry [1]. In 2050, approx. 4.6 Mio t calcined clays are foreseen as a cement main constituent in Germany [2].

With the expected introduction of calcined clays, issues such as the simplest possible storage without loss of reactivity, storage stability and transport will come into focus.

Little knowledge is available on the storage stability of calcined clays. Few studies were made about potential aging and weathering effects or the impact on its performance as an SCM [3]. The aging of the investigated mixed-layer clays had negligible influence on fresh mortar properties and strength of mortar made with these clays. However, they also showed new mineral formation depending to the atmosphere during storage and effects on the water demand. No reactivity development studies were performed. In order to gain knowledge about the storage sensitivity of calcined clays in different environments the influences of fineness, temperature and humidity on the

reactivity of a calcined clay were investigated in this study.

2 Methods and materials

2.1 Determination of moisture and water content

For the determination of moisture, the calcined clay samples were dried at 40 °C in a muffle oven. The weight loss after drying was attributed to moisture.

The water content was determined by heating the previously dried sample to 950 °C in an ELTRA CW Multiphase.

2.2 X-ray diffraction

The mineralogical composition of the samples was examined by means of X-ray diffraction analysis (XRD). The samples were analysed at uniform fineness within a diffraction angular range of 5 – 65° 2 Theta using a Bruker D8 Advance. The X-ray diffraction pattern was evaluated quantitatively with the Rietveld refinement method using quartz content as an internal standard.

2.3 Determination of reactivity

The amount of reactive silicon dioxide was determined acc. EN 197-1.

Following the recommendation of the RILEM Group, the pozzolanic reactivity of the calcined clays was additionally determined acc. ASTM C1897-20 [4, 5]. The heat of hydration of the activated samples was determined after 72 and 168 h using isothermal heat flow calorimetry in a TAM-Air calorimeter.

2.4 Characterization of raw clay

The raw clay was identified as an illitic-kaolinitic clay with quartz as the main contamination (**Table 1**). The raw clay was analysed using combined methods of XRD; XRF and wet chemistry. Minor components are goethite, feldspars and carbonates.

Table 1 Mineral composition of raw clay in wt.%.

Mineral	raw clay	calcined clay
Quartz	ca. 25	ca. 25
Calcite	< 1	<0.5
Siderite	< 0,5	-
Feldspar	< 2	<2
Rutile	ca. 1	ca. 1
Illite / Mica	35-40	25-30
Kaolinite	20-25	-
Goethite	8-10	2-5
Hematite	-	2-5
Glass		30-35

The clay sample was calcined in a batch furnace at 700 °C for 30 minutes. After the calcination kaolinite was completely dehydroxylated, whereas illite and mica were only partly dehydroxylated (**Table 1**). The Carbonates were partially decomposed. The reference sample was analysed directly after calcination without storage time.

After calcination the sample was crushed to a size of < 10 mm in a jaw crusher (“g-samples”). Half of the sample was ground further to analytical fineness < 90 µm in a disc mill (“f-samples”).

2.5 Experimental set-up

Two sample series were created using the crushed coarse (“g”) and the finely ground (“f”) calcined clay (**Figure 1**). Three times 100 g of each sample were put into a glass beaker and stored for 7, 28 and 91 days at the following different conditions:

- at 20 °C sealed in a desiccator over silica gel (dry)
- at 20 °C and 65 % rel. humidity (20/65)
- at 40 °C and 100 % rel. humidity (40/100).



Figure 1 Sample for storage experiments. left: crushed coarse calcined clay (g); right: finely ground sample (f)

3 Results and discussion

3.1 X-ray diffraction

The X-ray diffraction analyses show no significant differences in the mineral content of the samples despite their different storage conditions and duration. Crystalline hydrate-phases were not formed during storage of the calcined clay.

3.2 Moisture at 40 °C

As expected, the moisture of the samples (f, g) stored in a desiccator at 20 °C remained almost unchanged during 91 days of storage.

Figure 2 show the moisture contents of the samples stored in climate chambers (20/65 and 40/100) compared to the original sample (reference). Stored at 20/65 both sample types showed

a small increase in moisture of approx. 1-1,5 wt.%. The moisture of both samples (f, g) did not increase further after 7 days. The finely ground samples (f) had minimal higher moisture contents than the coarser samples (g).

Samples stored at 40/100 had high moistures of about 15 wt.% after 7 days. After that storage time the moisture of the crushed samples (g) remained constant, whereas that of the fine sample (f) increased up to 30 wt.% (**Figure 2**). This is most probably caused by the larger adsorption capacity of the higher surface area.

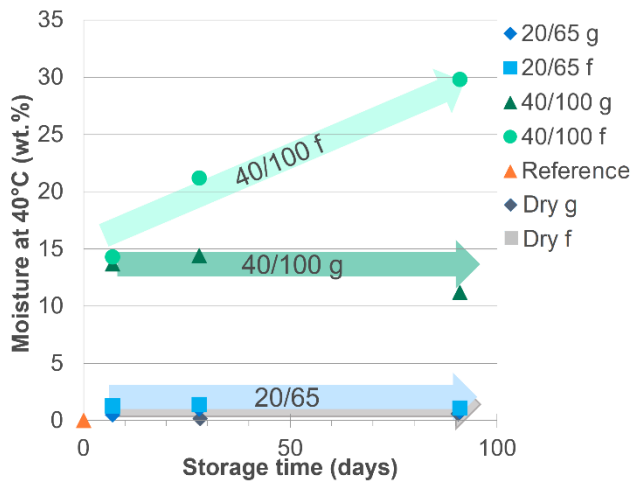


Figure 2 Moisture at 40 °C of samples stored in different climates for 7, 28 and 91 days. g = coarse crushed samples, f = finely-ground samples; 20°C/65%r.h.; 40°C/100%r.h.; 20°C over silica gel (dry)

3.3 Content of chemically bound water

The changes in water content of the calcined clays during storage are given in **Figure 3**. The water content of samples stored in the desiccator showed a slight increase of approx. 1 wt.% after 7 days compared to the reference sample. Small contents of free lime that were formed by the partial calcination of carbonates probably caused this increase due to its hydrophilic nature. At 91 days of storage a further increase of about 1 wt.% was observed. Samples stored at 20/65 had a comparable increase of their water content, at 91 days of storage their water content was about 3.5 wt.%. Both sample fractions stored at 40/100 are shown with about 4.5 wt.% the highest water contents at 91 days (**Figure 3**).

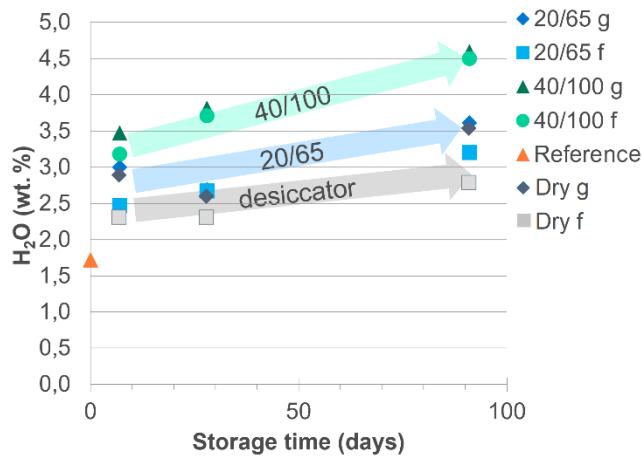


Figure 3 Chemically bound water g = coarse crushed samples, f = finely-ground samples; 20°C/65%r.h.; 40°C/100%r.h.; 20°C over silica gel (dry).

3.4 Reactivity

The amount of reactive SiO₂ acc. EN 197-1 of the samples stored in a desiccator or climate chambers (**Figure 4**) was changing depending on their fineness. In the environments (dry, 20/65 and 40/100) the amount of reactive SiO₂ of the coarse samples (g) was not affected within analytical error, whereas the fine samples (f) lost about 2.5 wt.% reactive SiO₂ compared to the reference sample. Apparently, the influence of storage on the amount of reactive silica depends predominantly on the particle size and less on the selected moisture and temperature conditions. The change in reactive silica over time might be attributed to aging processes on the micro scale.

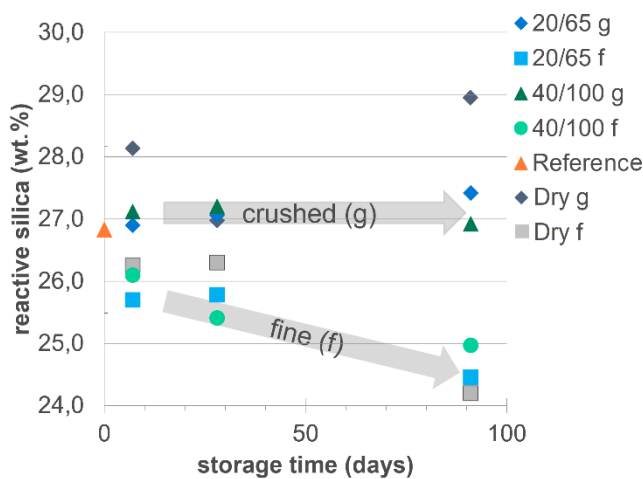


Figure 4 Reactive silica of samples stored in different climates for 7, 28 and 91 days. g = coarse crushed samples, f = finely-ground samples; 20°C/65%r.h.; 40°C/100%r.h.; 20°C over silica gel (dry)

Heat of hydration acc. ASTM C1897-20 was analysed on samples stored in a desiccator and in 40/100 climate (**Figure 5**) for 7- and 91-days storage time. Samples stored in the desiccator

showed a slight decrease in their heat of hydration over 91 days, whereas samples stored at 40/100 showed a stronger decline.

The decrease in reactivity concluded by the decrease in the heat of hydration is probably due to formation of amorphous hydrate phases. The crystalline mineral phases observed in x-ray diffraction did not change during storage time (3.1).

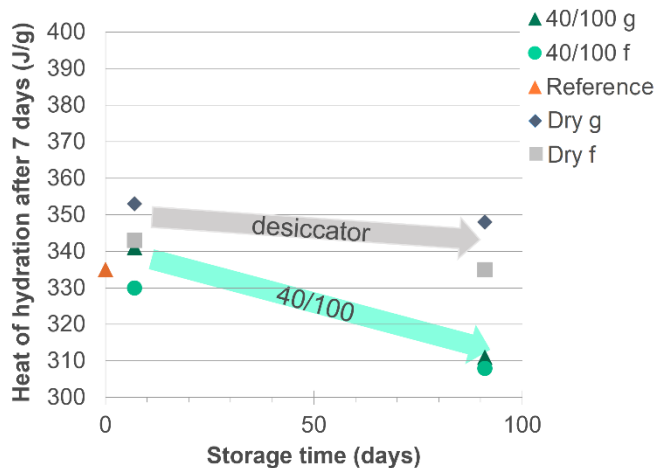


Figure 5 Heat of hydration of samples stored in different climates for 7 and 91 days. g = coarse crushed samples, f = finely-ground samples; 40°C/100%r.h.; 20°C over silica gel in desiccator (dry)

3.5 Conclusion and outlook

The storage stability of a coarse and a finely ground calcined clay was analysed in three different environmental conditions (desiccator, 20/65, 40/100).

It could be shown that finely ground samples are particularly sensitive to moisture absorption and loss of reactivity.

This study implicates, that calcined clays can be stored as coarse-grained fraction at normal conditions and do not require special storage conditions. They can certainly be stored outdoors, protected from moisture, without mineral reactions occurring or loss of reactivity. However, the results cannot be applied without restriction to all calcined clays and may vary depending on the clay type and its mineral composition.

References

- [1] Verein Deutscher Zementwerke, VDZ (2021) Decarbonising Cement and Concrete: a CO₂ Roadmap for the German cement industry. Düsseldorf. <https://vdz.info/dekarbonisierung>
- [2] Verein Deutscher Zementwerke, VDZ (2022) Resources of the future for cement and concrete – potential and action strategies. Düsseldorf
<https://www.vdz-online.de/ressourcenschonung>
- [3] Gmür, R., Thienel, K.-C., Beuntner, N., (2016) Influence of aging conditions upon the properties of calcined clay and its performance as supplementary cementitious material. Cement and Concrete composites 72, p 114-124-
- [4] Londono-Zuluaga, D., Gholizadeh-Vayghan, A., Winnefeld, F. et al. (2022) Report of RILEM TC 267-TRM phase 3: validation of the R3 reactivity test across a wide range of materials. Materials and Structure 55, pp.142.
- [5] ASTM C1897-20 (2020) Standard Test Methods for Measuring the Reactivity of Supplementary Cementitious Materials by Isothermal Calorimetry and Bound Water measurements. ASTM Int West Conshohocken.