



Influence of aging conditions upon the properties of calcined clay and its performance as supplementary cementitious material



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ARTICLE INFO

Article history:

Received 19 August 2015

Received in revised form

25 April 2016

Accepted 25 May 2016

Available online 27 May 2016

Keywords:

Calcined clay

Aging

Storage condition

Cement

Hydration

SCM

ABSTRACT

The investigation aimed at determining a possible impact of various aging conditions on calcined clays and their performance as supplementary cementitious material (SCM). Two calcined clays were exposed to six different aging conditions. Chemo-mineralogical and physical parameters were measured to reveal possible changes. Aging of calcined clays at high relative humidity or in 3% CO₂ atmosphere resulted in a higher specific surface area and an increased water demand. This was in part due to the formation of calcite and gypsum. The latter promoted the development of heat of hydration. The aging of calcined clays itself had negligible influence on fresh mortar properties and no clear effect on strength of mortar made with these SCM. Nonetheless, most flexural and compressive strength values of mixes containing 20% aged calcined clay were higher than the reference mixes made with cement only.

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1. Introduction

Global shortages of raw materials suitable as binder component in concrete and high carbon dioxide (CO₂) emission caused e.g. by cement production make innovations unavoidable in the building materials industry. In 2009, cement industry was responsible for 5% of total anthropogenic CO₂ emissions [1,2]. Hence, reducing the environmental impact of cement is an elementary approach for the years to come. The disposition of secondary resources, which have been used as concrete admixture so far, becomes more and more insecure due to the evolving production of alternative energy [3,4] or economic fluctuations [5] and can by no means supply further increasing needs. Especially due to economic growth in emerging countries like India or China, the demand for cement could increase up to 72% by 2050 compared to the reference year 2006 [1]. Thus, ecologically and financially sustainable supplementary cementitious materials (SCM) become increasingly interesting [6].

Calcined clays represent such an interesting alternative. According to DIN EN 197-1 [7], calcined clay is a naturally tempered pozzolan, which can be used e.g. as Type II addition in concrete [8]. During the last decades many studies focused on pure clays, e.g.

Refs. [9–13], looking into their individual reactivity and optimal calcination temperature. Most often metakaolin was investigated, since it is known for its high reactivity in cementitious systems [12,14–20]. More recently naturally occurring clay mixes came into focus. They contain in various amounts kaolinite, illite, montmorillonite and chlorite as main components [13,16,21–25]. Due to their mineralogical composition, these raw clays are hardly attractive for other industries and thus, no price competition has to be expected. Such raw clays are available worldwide, short transport distances are guaranteed and shortages depending on market conditions will not occur. Calcination of clay can be easily accomplished in existing productions lines [21,26–28]. Beside economical advantages, they are also attractive ecologically since they contain usually only small amounts of calcium carbonate. While the calcination of the calcium carbonate during cement clinker production causes high CO₂ emissions (0.785 tons CO₂ per ton cement [29]), calcined clays suitable as SCM can reduce the material immanent CO₂ emissions since they produce only as much as 0.022 tons CO₂ per ton calcined clay in case of a Lias Delta [26].

Thus far the impact of calcined clay as SCM upon mortar or concrete properties had been investigated only using freshly calcined and promptly ground clays, whereat the chronological order often is reversed. The impact on strength properties differed depending on the type of clay, the calcination temperature and regime as well as the fineness of the calcined clay [13,23,26,30–32].

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In most cases calcined clays reduced the water/binder ratio due to their high water demand. As a result, mortars using a 20–30% replacement of kaolinitic clay as SCM exceeded significantly the strength of the references made with cement only. Few researchers investigated the impact of calcined clays as SCM upon workability of fresh mortar [26,33–35] or shrinkage behavior of hardened mortar [26].

This paper focuses on the possible impact of the different aging conditions of calcined clay produced on industrial scale [21,26]. Optimal storage and prompt application of binders is aimed at in industry yet often not feasible in practice. For this reason, it is desirable that calcined clays feature insensitiveness to long-term storage and environmental influences, especially carbonation and higher moisture content of the air. The objective of the research was to investigate a possible impact of aging and to refer to known aging effects of cement and other SCM, e.g. blast furnace slag.

Cement changes its material properties due to high relative humidity or CO₂-rich atmosphere. H₂O molecules are adsorbed and form a nm-thin layer of hydration products on the surface of clinker phases thereby increasing the specific surface area of the cement [36]. A higher water demand and consequently a reduced flowability go along with this higher specific surface area [37]. A negative impact on workability of prehydrated cement due to agglutination was also observed [38]. In addition, Dubina and Plank [37] investigated the reactivity of prehydrated cement. A higher solubility of sulfate ions increased the formation of ettringite in C₃A-rich prehydrated cement. As consequence, the hydration heat ergo the reactivity of the aged cement was lower compared to unhydrated cement [37,39].

The influence of aging conditions on the properties of blast furnace slag is discussed controversially [40–46]. It was reported that aging has a rather negative impact on the reactivity of blast furnace slag, as the latent-hydraulic properties seemed to diminish [40,41]. On the other hand, a higher reactivity potential of aged blast furnace slag was determined [44]. After natural weathering of blast furnace slag, hydration products (CSH-phases) and calcite crystals were detected on the slag's surface but they had no influence on its reactivity in cementitious systems [43]. Hence, no significant differences between fresh and aged blast furnace slag were detected. Frigione and Sersale [45] and Mußgnug [46] observed a loss of strength in mortar systems with aged blast furnace slag, while Görtz and Trettin [42] determined even a strength increase in mortar containing aged blast furnace slag.

For the investigation at hand two calcined clays differing in their calcination temperature were exposed to various aging conditions in order to analyze the impact of humidity, temperature and CO₂ content of the air on the properties of the calcined clays as such and the resulting impact on workability and strength of mortar produced with these artificially aged calcined clays.

2. Materials and methods

2.1. Materials

The raw clay originates geologically from a Lias Delta layer (Pliensbachian Lower Jurassic). It was extracted from a clay pit in Unterstürmig, Franconia, Germany. Mixed layer clay with low kaolinite content (Table 3) had been crushed coarsely to a maximum particle size of approximately 100 µm right after its delivery and subsequently fed into a tripartite rotary kiln normally used for the production of expanded clay. Clay was calcined in two batches at maximum temperatures of 850 °C (designation: CT1) and 750 °C (CT5). During this process, both calcined clays were exposed to a combined impact of temperature and moisture gradients [21,26]. Hence, the following test methods respect not only

the impact of different aging conditions but also different calcination temperatures on potential aging effects. The combined hygrothermal impact together with the mechanical action while passing through the rotary kiln reduced the size of the particles. Thus the resulting calcined clay particles had a smaller maximum size of up to 40 µm. The type of grinding equipment used for both calcined clays was the second difference between them besides the calcination temperatures. While CT1 was ground in an industrial ball mill, CT5 was ground in an industrial roller mill. This trial on industrial scale had no impact on the results presented here.

An ordinary Portland cement CEM I 32.5 R, complying with the European Standard EN 197-1 [7], was used for mortar tests.

Chemical analysis of the raw clay was carried out by X-ray fluorescence (XRF) using a Bruker S2 Ranger. The cement producer provided the chemical analysis of the cement and its potential compound composition. Table 1 contains the chemical composition data for the materials used.

Particle density was determined by a gas pycnometer (Helium Pycnomatic ATC, ThermoFisher Scientific). Specific surface areas of raw materials were measured according to DIN ISO 9277 (BET-method) [47] by means of an analyzer SA-9601 MP (Horiba Instruments Inc.). Samples were pre-treated at 200 °C under a nitrogen flow before the measurements were started. Water demand of the calcined clays was determined according to Puntke [48]. The method determines the densest particle package by the minimum water demand needed for saturating a powder like pulverized limestone or ground calcined clay. As long as the powder is moistened but unsaturated, the adjustment of the particles is prevented due to capillary tension. By adding water dropwise to the sample, the exact saturating point is found, for which capillary tension is lost and the void volume is minimized. These tests were always triplicated and according to Puntke [48] the lowest water demand is relevant. The reaction potential was assessed in a 20-h elution test. In each case 1 g of calcined clay was dispensed in 400 ml of ten percent sodium hydroxide. The resulting concentrations of soluble silicon and aluminum ions were determined subsequently with the help of inductively coupled plasma - optical emission spectroscopy (ICP-OES) [49]. Table 2 lists the physical properties of the three basic test materials together with the soluble amounts of Al- and Si-ions released from the calcined clays.

Particle size distribution was determined in a laser diffraction sizing instrument Horiba LA-950 after preceding dispersion in isopropanol by ultrasonic treatment for 1 min. Fig. 1 shows the

Table 1
Chemical analysis of test materials [%] by weight.

Oxides	Portland cement ^a	Raw clay
SiO ₂	19.3	52 ± 2
Al ₂ O ₃	4.6	21 ± 1
CaO	57.5	3 ± 1
Fe ₂ O ₃	2.9	8 ± 1
MgO	0.8	2 ± 0.5
K ₂ O	0.7	3 ± 1
Na ₂ O	0.1	0.4 ± 0.1
SO ₃	2.6	1 ± 0.5
TiO ₂	0.2	1 ± 0.5
Na ₂ O equivalent	0.6	
Bogue potential compound ^a		
C ₃ S		52
C ₂ S		18
C ₃ A		7
C ₄ AF		9

^a Information provided by the producer.

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