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Influence of kaolinite crystallinity and calcination conditions on the pozzolanic activity of metakaolin

Introduction

Pozzolan, a siliceous or siliceous and aluminous material, slowly reacts with $\text{Ca}(\text{OH})_2$ in the finely divided form at an ordinary temperature in the presence of moisture to form compounds possessing cementitious properties, which refines pore size distribution and enhances mechanical properties and durability (ASTM C618:2013; Tironi et al. 2013, 2014). The incorporation of pozzolans into mortar and concrete enhances its various properties and simultaneously decreases cement dosage, leading to the remarkable reduction of CO_2 emission and energy consumption, which is eco-friendly and thus encouraged by the government (Tironi et al. 2012).

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Kaolinite, a layered silicate mineral that occurred in kaolin ores, loses its OH lattice water during calcination at 500–900°C and then converts into amorphous metakaolinite (Janotka et al. 2010). During the transformation of kaolinite into metakaolinite, the Si–O network remains largely intact and Al–O network reorganizes itself, which switches to a highly disordered amorphous structure (Kakali et al. 2001). Kaolinite exhibits no pozzolanic activity due to its stable crystal structure, while metakaolinite, which possesses a highly disordered structure, can react particularly well with $\text{Ca}(\text{OH})_2$ produced by cement hydration in the presence of moisture and then form the additional C–S–H, C–A–H and C–A–S–H gels (Murat 1983). Therefore metakaolinite can be concerned as an active pozzolan with high pozzolanic activity.

The pozzolanic activity of metakaolinite is mainly related to the calcination condition (Badogiannis et al. 2005; Cao et al. 2016), fineness of the product (Samet et al. 2007), purity and crystallinity of the original kaolinite (Bich et al. 2009). In brief, calcination conditions, including calcination temperature, holding time, heating and cooling rate, destroy crystal structure and greatly impact the timing, speed and degree of kaolinite dehydroxylation, while the fineness of the product has a large influence on the dehydroxylation rate of kaolinite and the pozzolanic reaction rate between $\text{Ca}(\text{OH})_2$ and metakaolinite. Apart from the purity of original kaolinite, it is almost linearly related to pozzolanic activity and the crystallinity of original kaolinite also affects the dehydroxylation process and pozzolanic reaction that kaolinite with high crystallinity converts into less active metakaolinite reported by Kakali et al. (Kakali et al. 2001).

The pozzolanic activity of metakaolinite was assessed by a wide range of test methods, which are divided into direct and indirect methods (Donatello et al. 2010). The direct methods contain a modified Chapelle test and Frattini test, which monitor $\text{Ca}(\text{OH})_2$ content directly by analytical methods, and then $\text{Ca}(\text{OH})_2$ consumption is calculated in time to represent pozzolanic activity (EN 196-5:2005; NF P18-513:2010; Ferraz et al. 2015). The indirect methods determine compressive strength, electrical conductivity or the heat evolution of cement solutions pastes or mortars incorporating with metakaolinite, which indirectly reflect the extent of pozzolanic activity (Frías et al. 2000; EN 196-1:2005; Sinthaworn and Nimityongskul 2011).

In this paper authors selected two kaolin ores with almost the same fineness and purity of original kaolinite to research the influence of crystallinity and calcination conditions on the pozzolanic activity of metakaolin samples. The different calcination conditions were conducted by altering calcination temperature and holding time to obtain metakaolin samples with different degrees of dehydroxylation. The crystallinity of kaolinite was characterized by the Hinckley Index (HI) based on XRD patterns (Qiu et al. 2014). Then pozzolanic activities of metakaolin samples with different crystallinity and degree of dehydroxylation were assessed by a modified Chapelle test, Frattini test and strength evaluations. Additionally, the influence of kaolinite crystallinity on dehydroxylation was evaluated by TG analysis followed by the calculation of apparent activation energies.

1. Materials and methods

1.1. Materials

Two kaolin ores with low and high crystallinity (abbreviated as KL and KH, respectively) studied in this paper were collected from kaolin deposits associated with coal in Yichang City (Province of Hubei, China). The chemical compositions of kaolin ores detected by XRF (Table 1) showed that the main constituents of KL and KH were SiO_2 (> 47 wt.%) and Al_2O_3 (> 33 wt.%) accompanied by some minor impurities such as Fe, Ti, S, Ca and K (total oxide content < 5%). XRD patterns of KL and KH (Figure 1) exhibited the presence of kaolinite as the main mineral in each sample, and KL presented some weak diffraction peaks of impurity minerals (quartz, anatase, boehmite and pyrite). Combined with XRF and XRD data, the mineralogical compositions of kaolin ores were evaluated by the following steps:

- ◆ the content of kaolinite was evaluated as the ratio of Al_2O_3 value of KL and KH in XRF analysis to the theoretical Al_2O_3 value of kaolinite (39.5%),
- ◆ the content of quartz was evaluated as the SiO_2 value of KL and KH in XRF analysis minus SiO_2 content of kaolinite,
- ◆ the content of carbonaceous matters was evaluated as LOI minus H_2O content of kaolinite.

Table 1. Chemical compositions of kaolin ores (mass %)

Tabela 1. Skład chemiczny rud kaolinu (% masowy)

Oxide	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	SO_3	K_2O	LOI
KL	47.30	33.89	2.15	0.93	0.07	1.02	0.28	14.07
KH	50.75	33.51	1.19	0.31	0.11	0.08	0.02	13.63

The obtained mineralogical compositions data (Table 2) were approximate due to the neglect of Al_2O_3 derived from boehmite and LOI derived from pyrite. The results have shown that the amount of kaolinite was almost the same between KL and KH, while the characteristic diffraction peaks of kaolinite in KH were almost twice the KL's intensity, and diffraction peak shape of KH was sharper than that of KL, demonstrating the higher crystallinity of KH. KH contained a higher content of quartz accompanied by a higher SiO_2 and Si/Al ratio. The content of carbonaceous matters showed that about 2% of carbonaceous matters were introduced into kaolin deposits.

The crystallinity of kaolinite can be characterized e.g. by Hinckley Index (HI) (Galos 2011). It is defined as the ratio between the summation of height above the background of (1 $\bar{1}$ 0) and (11 $\bar{1}$) reflections to the total height of (1 $\bar{1}$ 0) (Figure 1) (Qiu et al. 2014). It is reported that kaolinite was classified as highly ordered, ordered, disordered, highly disordered

corresponding to $HI > 1.3$, $1.1 \sim 1.3$, $0.8 \sim 1.1$, < 0.8 (Liu et al. 2000). The results (Table 2) showed that HI of KL (0.71, highly disordered) was half less than KH (1.65, highly ordered), demonstrating the lower crystallinity of KL. Moreover, the particle size distributions of KL and KH (Table 2) were almost the same due to the same crushing and grinding procedures using the same equipment in a plant.

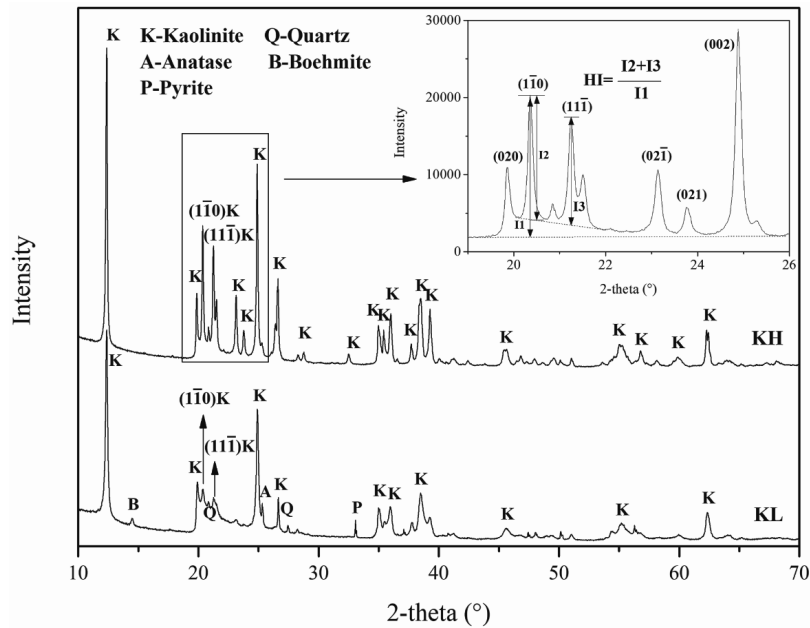


Fig. 1. XRD patterns of KL and KH

Rys. 1. Dyfrakcja rentgenowska (XRD) dla rud kaolinu oznaczonych symbolami KL i KH

Table 2. Mineralogical compositions, crystallinity and particle size of kaolin ores

Tabela 2. Skład mineralogiczny, krystaliczność i wielkość cząstek rud kaolinowych

Kaolin	KL	KH
Kaolinite (wt.%)	~84	~85
Quartz (wt.%)	~8	~11
Si/Al ratio	2.37	2.57
Carbonaceous matters (wt.%)	~2.4	~1.8
HI	0.71	1.65
d_{25} (μm)	3.48	3.40
d_{50} (μm)	12.65	12.55
d_{75} (μm)	28.78	26.68

1.2. Apparent activation energy calculation

The isoconversional methods, Ozawa method (Ozawa 1965) and Kissinger–Akahira–Sunose method (Kissinger 1957; Akahira and Sunose 1969), have been used to calculate the apparent activation energies of kaolinite dehydroxylation processes for the two kaolin ores with different heating rates (10, 20 and 30 K/min). The analysis errors of isoconversional methods have been remarkably reduced by iterative calculations to approach the exact values of apparent activation energies (Gao et al. 2001).

1.3. Calcination

The calcination of kaolinite in the temperature range of 500–900°C caused the dehydroxylation in the crystal structure, resulting in the generation of metakaolinite, which could be considered as a pozzolan. The calcination treatments of KL and KH samples were conducted at different temperatures and holding times (Table 3) under the air atmosphere after drying at 105°C for 2 h to remove the absorbed water in the pores and layers. The obtained metakaolin samples after calcination were noted as MKLi and MKHi ($i = 1-11$). The weights of samples before and after calcination were collected and then the mass loss rates were calculated to evaluate the degree of dehydroxylation according to equations (1) and (2), whose results were also exhibited in Table 3.

$$\text{Mass Loss Rate (MLR, \%)} = \frac{W_0 - W_1}{W_0} \cdot 100\% \quad (1)$$

$$\text{Degree of Dehydroxylation (\%)} = \frac{MLR - W_{CB}}{LOI - W_{CB}} \cdot 100\% \quad (2)$$

- W_0 – the weight of the sample before calcination, %;
- W_1 – the weight of the sample after calcination, %;
- MLR – mass loss rate in equation (1), %;
- W_{CB} – the weight of carbonaceous matters (Table 2), %;
- LOI – the loss on ignition (Table 1), %.

As showed in Table 3, it is found that dehydroxylation of KH was more difficult than that of KL. That is to say, under the same calcination conditions, the degree of dehydroxylation of KL was always higher than that of KH.

Table 3. Calcination conditions, mass loss rate and degree of dehydroxylation

Tabela 3. Warunki kalcynacji, szybkość utraty masy i stopień dehydroksylacji

Kaolin	Metakaolin	Temperature (°C)	Holding time (h)	Mass loss rate (%)	Degree of dehydroxylation (%)
KL	MKL1	500	1	4.6	19
	MKL2	500	3	8.1	49
	MKL3	500	4	9.8	64
	MKL4	600	0.5	6.0	31
	MKL5	600	2	12.9	90
	MKL6	700	0.5	10.7	70
	MKL7	700	2	13.6	96
	MKL8	800	0.5	13.3	94
	MKL9	800	2	14.0	100
	MKL10	900	0.5	14.0	100
	MKL11	900	2	14.0	100
KH	MKH1	500	3	4.7	25
	MKH2	500	4	6.6	41
	MKH3	600	1	8.4	56
	MKH4	600	2	10.5	74
	MKH5	600	4	12.6	91
	MKH6	700	1	9.7	67
	MKH7	700	2	12.4	90
	MKH8	800	0.5	11.7	84
	MKH9	800	2	13.6	100
	MKH10	900	0.5	13.6	100
	MKH11	900	2	13.6	100

1.4. Pozzolanic activity of metakaolin

Pozzolanic activities of metakaolin samples (MKL1–11 and MKH1–11) were characterized by the modified Chapelle test (NF P18-513:2010), Frattini test (EN 196-5:2005) and strength evaluations (EN 196-1:2005).

The modified Chapelle test was conducted by measuring the non-reacted lime after extracting the reaction solution of 1 g metakaolin and 2 g CaO in 250 ml deionized water

at 90°C for 16 h by a sucrose solution and then pozzolanic activities were expressed in mg Ca(OH)₂ consumed by 1g metakaolin (mg/g).

The Frattini test was prepared by mixing 16 g Portland cement with 4 g metakaolin into 100 mL freshly boiled deionized water and then placed into a sealed polyethylene container for 3, 7 and 28 days in an oven at 40°C. Then [CaO] and [OH] were measured by titration with 0.03 mol/L EDTA and 0.1 mol/L HCl after filtering and drying. The test results of metakaolin samples were compared with the solubility curve of Ca(OH)₂ at 40°C and then metakaolin can be classified as an active pozzolan when its [CaO] and [OH] in the solution is located down the solubility isotherm.

Compressive strengths of blended cement mortars containing 12 wt.% metakaolin samples were assessed on cubes (4 × 4 × 16 cm³) made with standard sand (1:3) and water/blended ratio of 0.5 after curing at 20°C with 95% humidity for 3, 7 and 28 days.

2. Results

2.1. Apparent activation energy of kaolinite dehydroxylation

There is a strong characteristic mass loss in the TG curve corresponding to an endothermic peak in the DSC curve (400–800°C) belonging to the dehydroxylation of pure kaolinite (Zhang et al. 2015). The TG and DTG curves (350–850°C) of KL and KH with different heating rates (10, 20, 30 K/min) were displayed in Figure 2(a) and (b), respectively. The results showed that mass loss (about 12–13%) started at ~350°C and ended at ~850°C. Ahead of the initial dehydroxylation, the temperature (400°C → 350°C) might be due to the combustion of carbonaceous matters which was derived from associated coal in kaolin deposits and thus the combustion of carbonaceous matters also slightly contributed to mass loss in 350–850°C except for kaolinite dehydroxylation. The *x*-axis and *y*-axis values of the DTG peak, standing for maximum mass loss temperature and rate, have shown an increasing trend at a rising heating rate, revealing that a large heating rate would cause rapid dehydroxylation but a delay of maximum mass loss temperature, which was also confirmed by TG curves. With the same heating rate, the *x*-axis DTG peak value of KL was 15–21°C lower than that of KH, demonstrating that KL's kaolinite, which had lower crystallinity, was more easily dehydroxylated than KH's.

The apparent activation energies of kaolinite dehydroxylation were calculated by Ozawa method and Kissinger–Akahira–Sunose (KAS) method followed by iterative processing to gradually reach the exact value and the reaction mechanism function has been ignored in these used methods. Table 4 displayed the apparent activation energies of KL and KH at different conversion α (0.2–0.8) and the results have shown that apparent activation energies of KL were lower than that of KH at the same conversion α (0.3–0.8). Moreover, the average apparent activation energies of KL and KH were 174.47 and 191.52 kJ/mol, showing

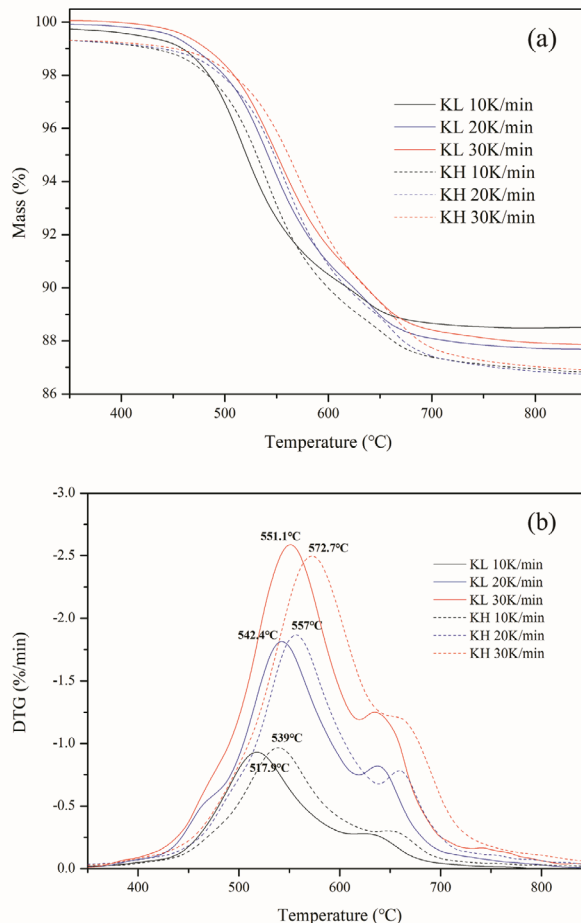


Fig. 2. TG (a) and DTG (b) curves of KL and KH in the temperature range of 350–850°C under different heating rates (10, 20, 30 K/min)

Rys. 2. Krzywe TG (a) i DTG (b) KL i KH w zakresie temperatur 350–850°C przy różnych szybkościach ogrzewania (10, 20, 30 K/min)

a difference value of ~ 17 kJ/mol. The apparent activation energy of kaolinite dehydroxylation has been reported to vary from 140 to 300 kJ/mol (Saikia et al. 2002) and that of the studied kaolin ores is close to the range. The lower average apparent activation energy of KL was expected due to the presence of highly disordered kaolinite what favored the removal of the structural hydroxyls, which was also confirmed by the lower temperature of DTG peak as shown in Figure 2. At $\alpha = 0.2$ – 0.25 , the abnormal phenomenon was observed that apparent activation energies of KL were higher than that of KH. The reason might be that KL's kaolinite lost the hydroxyls earlier, leading to the lower temperature than that of KH at the same conversion, which presented a higher apparent activation energy for KL at $\alpha = 0.2$ – 0.25 .

Table 4. Apparent activation energies (kJ/mol) of KL and KH at different conversion α (0.2–0.8)Tabela 4. Pozorne energie aktywacji (kJ/mol) KL i KH przy różnej konwersji α (0,2–0,8)

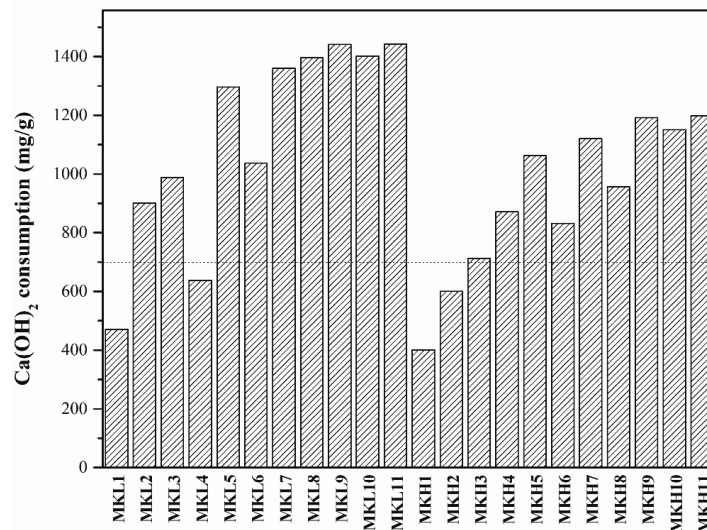
α	KL				KH			
	Ozawa-2	Ozawa-3	KAS-1	KAS-2	Ozawa-2	Ozawa-3	KAS-1	KAS-2
0.2	216.99	216.99	216.99	216.99	200.74	200.73	200.77	200.73
0.25	201.08	201.08	201.08	201.08	198.02	198.01	198.04	198.01
0.3	189.13	189.12	189.13	189.12	194.78	194.78	194.79	194.78
0.35	182.22	182.21	182.21	182.21	188.21	188.21	188.19	188.21
0.4	175.74	175.74	175.74	175.74	188.22	188.22	188.17	188.22
0.45	173.26	173.25	173.25	173.25	185.19	185.18	185.15	185.18
0.5	167.86	167.85	167.85	167.85	185.23	185.23	185.20	185.23
0.55	164.74	164.73	164.73	164.73	182.67	182.66	182.64	182.66
0.6	160.72	160.71	160.71	160.71	180.72	180.71	180.69	180.71
0.65	158.85	158.84	158.84	158.84	185.12	185.11	185.10	185.11
0.7	157.57	157.56	157.56	157.56	187.45	187.44	187.45	187.44
0.75	156.14	156.13	156.13	156.13	196.77	196.77	196.79	196.77
0.8	163.89	163.87	163.88	163.87	216.70	216.69	216.77	216.69
\bar{E}_a	174.48	174.47	174.47	174.47	191.53	191.52	191.52	191.52

Numbers of Ozawa-2, KAS-1 mean iteration times.

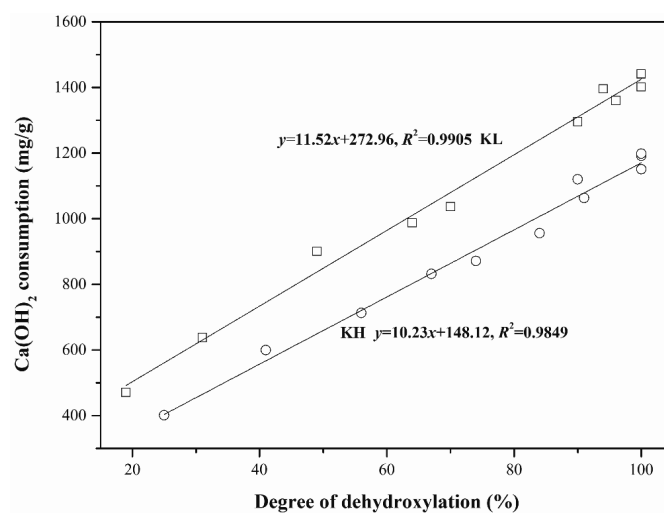
2.2. Pozzolanic activity of metakaolin

2.2.1. Modified Chapelle test

Figure 3 has shown $\text{Ca}(\text{OH})_2$ consumption in the modified Chapelle test to represent the pozzolanic activity of metakaolin. More $\text{Ca}(\text{OH})_2$ consumption represented more pozzolanic activity of metakaolin, leading to more performance enhancement with the replacement of metakaolin into cement pastes and mortars. Comparing with $\text{Ca}(\text{OH})_2$ consumption values of MKL and MKH, the maximum value of MKL was ~240 mg more than that of MKH, indicating that metakaolin with more pozzolanic activity was obtained by the dehydroxylation of kaolin with lower kaolinite crystallinity. According to French standard NF P18-513 (2005), metakaolin could be regarded as an active pozzolan when $\text{Ca}(\text{OH})_2$ consumption value > 700 mg/g. As observed in Figure 3, $\text{Ca}(\text{OH})_2$ consumption values of MKL1, MKL4, MKH1 and MKH2 were less than 700 mg/g, belonging to the non-active products, while other samples could be concerned as active pozzolans due to these values varied from 713 to 1442 mg/g.

Fig. 3. Ca(OH)₂ consumption of MKL and MKH samples in the modified Chapelle testRys. 3. Zużycie Ca(OH)₂ w próbkach MKL i MKH w zmodyfikowanym teście Chapelle'a

Also, Ca(OH)₂ consumption of MKL and MKH showed an approximate linear increasing trend (Figure 4) at a rising degree of dehydroxylation (Table 3). The coefficient R^2 of the fitting plot (Ca(OH)₂ consumption vs. degree of dehydroxylation) was 0.9905 and 0.9849 for MKL and MKH respectively, indicating well dependency. Moreover, the cut-off Ca(OH)₂

Fig. 4. The fitting plots of Ca(OH)₂ consumption vs. degree of dehydroxylationRys. 4. Wykres dopasowania zużycia Ca(OH)₂ w funkcji stopnia dehydroksylacji

consumption values of 700 mg/g were calculated based on the fitted equations and the corresponding degrees of dehydroxylation were about 37% and 54% for MKL and MKH, respectively. This meant that if the degree of dehydroxylation was less than the cut-off point, the calcination products presented no pozzolanic activity. Apart from the non-active products, the other samples could be classified as active pozzolans and the maximum pozzolanic activity was obtained at the optimal condition (800°C for 2 h), whose corresponding degrees of dehydroxylation were ~90%. Finally, the initial and optimal calcination conditions to obtain high active pozzolans from KL and KH were as follows:

- ◆ for KL, initial condition: 600°C for 2 h; optimal condition: 800°C for 2 h,
- ◆ for KH, initial condition: 600°C for 4 h or 700°C for 2 h; optimal condition: 800°C for 2 h.

In conclusion, the calcination conditions of kaolin and the maximum pozzolanic activity of calcination products were influenced by the crystallinity of kaolinite. That is to say, with lower crystallinity, KL could reach higher $\text{Ca}(\text{OH})_2$ consumption with lower calcination temperature or shorter holding time, while KH is just the opposite.

2.2.2. Frattini test

The plots of $[\text{CaO}]$ vs. $[\text{OH}]$ detected in the Frattini test for MKL (Figure 5) and MKH (Figure 6) were obtained to compare with the $\text{Ca}(\text{OH})_2$ solubility curve to distinguish pozzolanic activity. If the point of one sample is down solubility isotherm (located in the active region), it could be regarded as an active pozzolan. Meanwhile, higher pozzolanic acti-

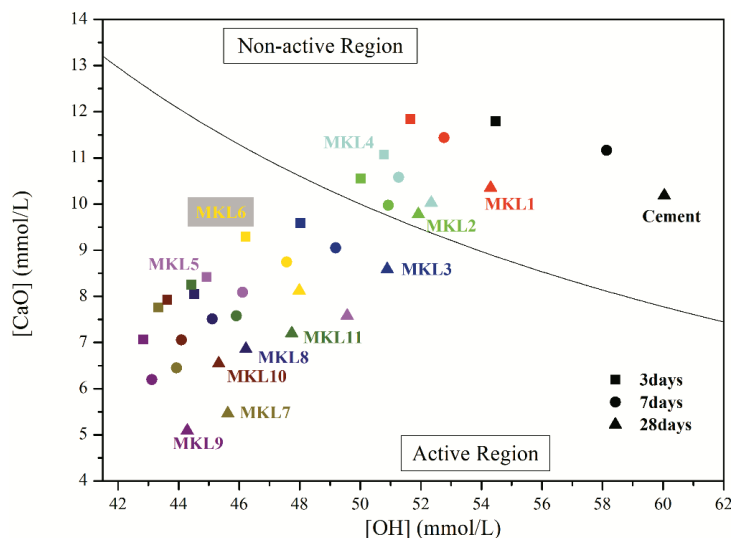


Fig. 5. The plot of $[\text{CaO}]$ vs. $[\text{OH}]$ in the Frattini test for MKL at 3, 7 and 28 days

Rys. 5. Wykres $[\text{CaO}]$ vs. $[\text{OH}]$ w teście Frattiniego dla MKL po 3, 7 i 28 dniach

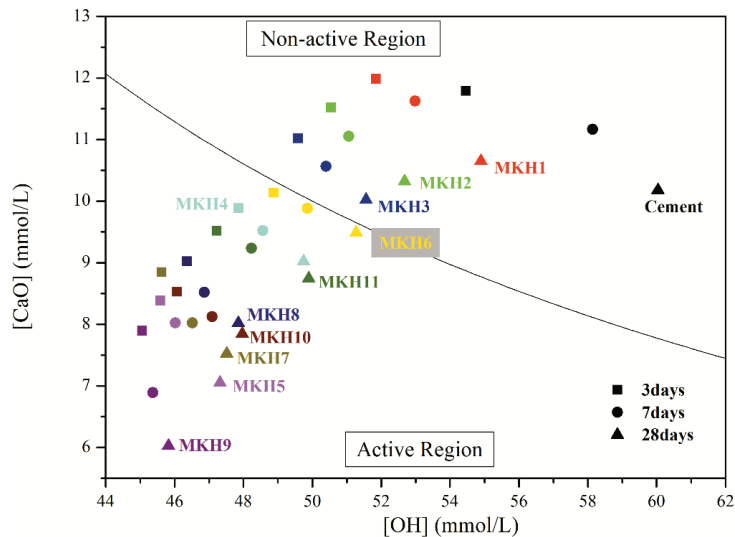


Fig. 6. The plot of [CaO] vs. [OH] in the Frattini test for MKH at 3, 7 and 28 days

Rys. 6. Wykres [CaO] vs. [OH] w teście Frattiniego dla MKH po 3, 7 i 28 dniach

vity was accompanied by the effective consumption of Ca^{2+} and OH^- released by cement hydration, which corresponds to the lower value of [CaO] and [OH] in the Frattini test. In Figure 5 and 6, cement, MKL1, MKL2, MKL4, MKH1, MKH2 and MKH3 samples were located in the non-active region, while others were located in the active region. Interestingly, MKL2 and MKH3 samples consumed more than 700 mg/g $\text{Ca}(\text{OH})_2$ in the modified Chapelle test but were located in the non-active region in the Frattini test, which was contradictory when evaluating their pozzolanic activity. The possible reasons will be discussed in section 3.

The general variation trend of pozzolanic activity accorded closely with that in the modified Chapelle test except for these metakaolin samples (MKL10, MKL11, MKH10 and MKH11) with the calcination temperature of 900°C, whose pozzolanic activities have shown a decreased trend as holding time prolonged. This abnormal phenomenon might be due to the fact that recrystallization products (mullite or spinel phase) which were initially formed at ~900°C and didn't react with $\text{Ca}(\text{OH})_2$, leading to the reduction of pozzolanic activity.

Compared with [CaO] and [OH] data of MKL and MKH, it is found that MKL consumed a larger amount of Ca^{2+} and OH^- released by cement hydration than MKH on the optimal condition and the amount difference of [CaO] and [OH] was ~1 and ~2 mmol/L, respectively. This result was consistent with that in the modified Chapelle test.

2.2.3. Strength evaluations

The incorporation of metakaolin samples into cement mortars would enhance the compressive strength by the mixture roles of dilution, physical and chemical effects (Wild et al. 1996; Sabir et al. 2001; Cyr et al. 2006). The dilution effect would decrease strength in proportion to the replacement level in all the curing ages. The physical effect would enhance strength due to the acceleration of cement hydration by the finer metakaolin particles, which provided large amounts of active heterogeneous nucleation sites. The chemical effect could also enhance strength caused by the strong pozzolanic reaction between metakaolin and $\text{Ca}(\text{OH})_2$ but the active time of the chemical effect was later than that of the physical effect and the maximum enhancement occurred between 7 and 14 days. The strength variations of cement mortars incorporating 12 wt.% MKL and MKH samples in the curing ages of 3, 7 and 28 days are displayed in Figures 7 and 8, respectively.

The compressive strength at 3 days had no obvious difference among all the mortars due to physical effect played almost equal roles despite whether dehydroxylation was completed or not. While at 7 and 28 days, metakaolin samples with high pozzolanic activity remarkably enhanced compressive strength but the detrimental influence was observed when incorporating non-active samples into cement mortar, especially at 28 days. The total change trend with a variation of dehydroxylation degree was consistent with that in the Frattini test. Compared with strength enhancement by MKL and MKH, it is found that MKL presented 4.5 MPa and 3.9 MPa larger strength than MKH on optimal calcination conditions, which was the same as that in the modified Chapelle test and the Frattini test.

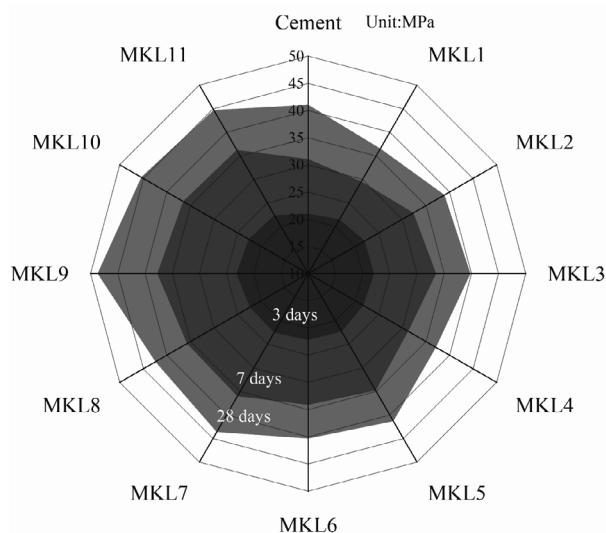


Fig. 7. Compressive strength evaluations of cement mortars incorporating MKL at 3, 7 and 28 days

Rys. 7. Ocena wytrzymałości na ściskanie zapraw cementowych zawierających MKL po 3, 7 i 28 dniach

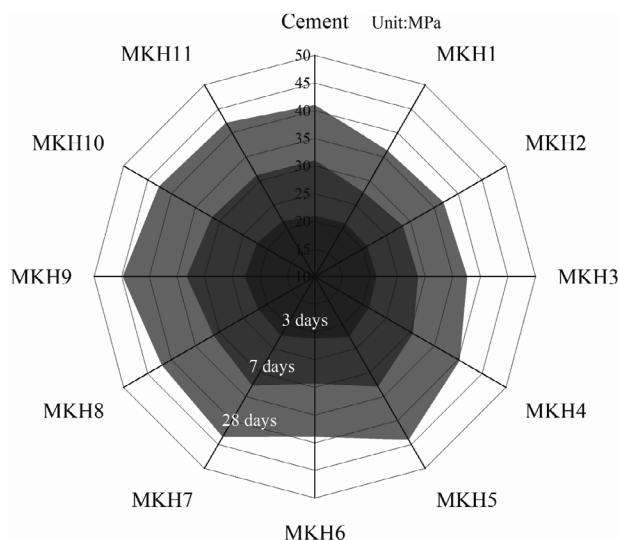


Fig. 8. Compressive strength evaluations of cement mortars incorporating MKH at 3, 7 and 28 days

Rys. 8. Ocena wytrzymałości na ściskanie zapraw cementowych zawierających MKH po 3, 7 i 28 dniach

3. Discussion

As mentioned in section 2.2.2, MKL2 and MKH3 samples consumed more than 700 mg $\text{Ca}(\text{OH})_2$, which could be regarded as an active pozzolan in the modified Chapelle test, but in the Frattini test they both were located in the non-active region and their strengths at 28 days were even less than that of pure cement mortar (blank test), indicating the absence of pozzolanic activity. This abnormal contradiction was possibly caused by different conditions of the three used assessment methods (showed in Table 5). The main factors affecting pozzolanic activity assessment methods were reaction temperature, surrounding substance and external intervention. In practice, the introduction of pozzolans into cement pastes, mortars and concretes was to enhance its various properties including compressive strength, so strength evaluation could be regarded as the standard method. Strength evaluation presented the slowest reaction rate under the lowest reaction temperature and the most stable surrounding (hardened mortar) with no external intervention, leading to the active time of the chemical effect (> 3 days) was longer than that in the Frattini test and the modified Chapelle test. In the Frattini test and the modified Chapelle test, a higher reaction temperature and water were conducted and mechanical agitation was even introduced into the modified Chapelle test, which accelerated the reaction rate to shorten the active time of the chemical effect to < 3 days (Frattini test) and < 16 h (modified Chapelle test). Compared with the results in strength evaluation tests, the dramatic reaction conditions in the modified Chapelle test caused the over-assessment of pozzolanic activity for the metakaolin samples

whose degrees of dehydroxylation were in the range of cut-off point to 90%. Nevertheless, the three used assessment methods accurately revealed change trends of pozzolanic activity and thus the combination of these methods was recommended in practice.

Table 5. Experimental conditions of the used assessment methods

Tabela 5. Warunki doświadczalne zastosowanych metod oceny

Method	Reaction temperature	Surrounding substance	External intervention	Active time
Strength evaluation	20°C	Hardened mortar curing at 95% relative humidity	None	> 3 days
Frattini test	40°C	Water	None	< 3 days
Modified Chapelle test	90°C	Water	Mechanical agitation	< 16 h

In general, kaolinite crystallinity remarkably affected activation and dehydroxylation of kaolin ores. To reach maximum pozzolanic activity, the activation of highly ordered kaolinite required a higher calcination temperature or longer holding time. Additionally, a higher apparent activation energy was also calculated in the dehydroxylation process. Afterward, the pozzolanic activity of the generated metakaolin sample was also greatly influenced by kaolinite crystallinity that metakaolin derived from high crystallinity kaolinite, which consumed less $\text{Ca}(\text{OH})_2$ and presented weaker compressive strength, demonstrating that the lower pozzolanic activity was obtained from the higher kaolinite crystallinity.

Conclusions

In this paper, two kaolin ores with almost the same fineness and purity of original kaolinite were selected to study the influence of original kaolinite crystallinity and calcination conditions on pozzolanic activity of the metakaolin samples tested by the modified Chapelle test, Frattini test and strength evaluations after dehydroxylation. The main conclusions are as follows.

The activation of kaolin ore was remarkably influenced by the crystallinity of original kaolinite. The lower crystallinity of kaolinite favored the removal of structural hydroxyls and required the lower calcination temperature or shorter holding time when reaching the same degree of dehydroxylation comparing with the highly ordered kaolinite. Consequently, the higher apparent activation energy was calculated for the highly ordered kaolinite and it would convert into less active metakaolinite during calcination, what is confirmed by the lower $\text{Ca}(\text{OH})_2$ consumption in the modified Chapelle test, higher $[\text{CaO}]$ and $[\text{OH}]$ in the Frattini test and weaker compressive strength.

Under different calcination conditions, metakaolin samples with a different degrees of dehydroxylation were obtained and conducted to assess pozzolanic activity. The results showed that pozzolanic activities were dependent on the degree of dehydroxylation except for samples calcined at 900°C where recrystallization processes started, and high pozzolanic activity was conducted by complete dehydroxylation (degree of dehydroxylation $\geq 90\%$).

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REFERENCES

- Akahira, T. and Sunose, T. 1969. Trans. Joint Convention of Four Electrical Institutes. Paper No. 246. Research Report, Chiba Institute of Technology (Science Technology) 16, pp. 22.
- ASTM C618:2013. Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete.
- Badogiannis et al. 2005 – Badogiannis, E, Kakali, G. and Tsvivilis, S. 2005. Metakaolin as supplementary cementitious material: Optimization of kaolin to metakaolin conversion. *Journal of Thermal Analysis and Calorimetry* 81(2), pp. 49–79.
- Bich et al. 2009 – Bich, C., Ambroise, J. and Péra, J. 2009. Influence of degree of dehydroxylation on the pozzolanic activity of metakaolin. *Applied Clay Science* 44(3), pp. 194–200.
- Cao et al. 2016 – Cao, Z., Cao, Y., Dong, H., Zhang, J. and Sun, C. 2016. Effect of calcination condition on the microstructure and pozzolanic activity of calcined coal gangue. *International Journal of Mineral Processing* 146, pp. 23–28.
- Cyr et al. 2006 – Cyr, M., Lawrence, P. and Ringot, E. 2006. Efficiency of mineral admixtures in mortars: quantification of the physical and chemical effects of fine admixtures in relation with compressive strength. *Cement and Concrete Research* 36, pp. 264–277.
- Donatello et al. 2010 – Donatello, S., Freeman-Pask, A., Tyrer, M. and Cheeseman, C.R. 2010. Effect of milling and acid washing on the pozzolanic activity of incinerator sewage sludge ash. *Cement and Concrete Composites* 32, pp. 54–61.
- EN 196-1:2005. Methods of Testing Cement. Part 1: Determination of strength.
- EN 196-5:2005. Methods of Testing Cement. Part 5: Pozzolanicity Test for Pozzolanic Cement.
- Ferraz et al. 2015 – Ferraz, E., Andrejkovičová, S., Hajjaji, W., Velosa, A.L., Silva, A.S. and Rocha, F. 2015. Pozzolanic activity of metakaolins by the french standard of the modified chapelle test: a direct methodology. *Acta Geodynamica et Geomaterialia* 179, pp. 289–298.
- Frías et al. 2000 – Frías, M., Sánchez de Rojas, M.I. and Cabrera, J. 2000. The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin-cement mortars. *Cement and Concrete Research* 30, pp. 209–216.
- Galos, K. 2011. Composition and ceramic properties of ball clays for porcelain stoneware tiles manufacture in Poland. *Applied Clay Science* 51(1), pp. 74–85.
- Gao et al. 2001 – Gao, Z., Nakada, M. and Amasaki, I. 2001. A consideration of errors and accuracy in the isoconversional methods. *Thermochimica Acta* 369, pp. 137–142.
- Janotka et al. 2010 – Janotka, I., Puertas, F., Palacios, M., Kuliffayová, M. and Varga, C. 2010. Metakaolin sand-blended-cement pastes: rheology, hydration process and mechanical properties. *Construction and Building Materials* 791, pp. 802–24.

- Kakali et al. 2001 – Kakali, G., Perraki, T., Tsivilis, S. and Badogiannis, E. 2001. Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity. *Applied Clay Science* 20, pp. 73–80.
- Kissinger, H.E. 1957. Reaction Kinetics in Differential Thermal Analysis. *Analytical Chemistry* 29(11), pp. 1702–1706.
- Liu et al. 2000 – Liu, Q., Xu, H. and Zhang, P. 2000. Crystallinity difference for various origin of kaolinities in coal measures. *Journal of China Coal Society* 25(6), pp. 576–580 (in Chinese).
- Murat, M. 1983. Hydration reaction and hardening of calcined clays and related minerals I. Preliminary investigation on metakaolinite. *Cement and Concrete Research* 13, pp. 259–266.
- NF P18-513:2010. Metakaolin. Pozzolanic addition for concrete. Definitions, specifications and conformity criteria.
- Ozawa, T. 1965. A New Method of Analyzing Thermogravimetric Data. *Bulletin of the Chemical Society of Japan* 38(11), pp. 1881–1886.
- Qiu et al. 2014 – Qiu, X., Lei, X., Alshameri, A., Wang, H. and Yan, C. 2014. Comparison of the physicochemical properties and mineralogy of Chinese (Beihai) and Brazilian kaolin. *Ceramics International* 40, pp. 5397–5405.
- Sabir et al. 2001 – Sabir, B.B., Wild, S. and Bai, J. 2001. Metakaolin and calcined clays as pozzolans for concrete: a review. *Cement and Concrete Composites* 23, pp. 441–454.
- Saikia et al. 2002 – Saikia, N., Sengupta, P., Gogoi, P.K. and Borthakur, P.C. 2002. Kinetics of dehydroxylation of kaolin in presence of oil field effluent treatment plant sludge. *Applied Clay Science* 22, pp. 93–102.
- Samet et al. 2007 – Samet, B., Mnif, T. and Chaabouni, M. 2007. Use of a kaolinitic clay as a pozzolanic material for cements: Formulation of blended cement. *Cement and Concrete Composites* 29(10), pp. 741–749.
- Sinthaworn, S. and Nimityongskul, P. 2011. Effects of temperature and alkaline solution on electrical conductivity measurements of pozzolanic activity. *Cement and Concrete Composites* 33, pp. 622–627.
- Tironi et al. 2012 – Tironi, A., Trezza, M.A., Irassar, E.F. and Scian, A.N. 2012. Thermal treatment of kaolin: effect on the pozzolanic activity. *Procedia Materials Science* 1, pp. 343–350.
- Tironi et al. 2013 – Tironi, A., Trezza, M.A., Scian, A.N. and Irassar, E.F. 2013. Assessment of pozzolanic activity of different calcined clays. *Cement and Concrete Composites* 37, pp. 319–327.
- Tironi et al. 2014 – Tironi, A., Trezza, M.A., Scian, A.N. and Irassar, E.F. 2014. Thermal analysis to assess pozzolanic activity of calcined kaolinitic clays. *Journal of Thermal Analysis and Calorimetry* 117, pp. 547–556.
- Wild et al. 1996 – Wild, S., Khatib, J.M. and Jones, A. 1996. Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete. *Cement and Concrete Research* 26, pp. 1537–1544.
- Zhang et al. 2015 – Zhang, Y., Xu, L., Seetharaman, S., Liu, L., Wang, X. and Zhang, Z. 2015. Effects of chemistry and mineral on structural evolution and chemical reactivity of coal gangue during calcination: towards efficient utilization. *Materials and Structures* 48, pp. 2779–2793.

INFLUENCE OF KAOLINITE CRYSTALLINITY AND CALCINATION CONDITIONS ON THE POZZOLANIC ACTIVITY OF METAKAOLIN

Keywords

kaolin, crystallinity, calcination conditions, pozzolanic activity

Abstract

Two kaolin ores with the almost same fineness and purity of original kaolinite but possessing different kaolinite crystallinity (Hinckley Index) were selected to study the influence of crystallinity and calcination conditions on the pozzolanic activity of metakaolin after dehydroxylation. The different calcination conditions were conducted by altering the calcination temperature and holding time to obtain different metakaolin samples with different degrees of dehydroxylation. Then pozzo-

lanic activities of metakaolin samples were tested by the modified Chappelle test, Frattini test and strength evaluations. Additionally, the apparent activation energies of two kaolin ores were calculated to study the thermal properties of kaolinite by isoconversional methods followed by iterative computations. The results showed that pozzolanic activities were dependent on the degree of dehydroxylation, except for the metakaolins calcined at 900°C due to the fact that recrystallization and high pozzolanic activity was conducted by complete dehydroxylation (degree of dehydroxylation $\geq 90\%$). Moreover, the lower crystallinity of original kaolinite favored the removal of the structural hydroxyls, leading to a reduction of apparent activation energy and increase of pozzolanic activity, indicating that the higher calcination temperature or longer holding time was required during calcination to reach the same degree of dehydroxylation and finally highly ordered kaolinite converted into the less active metakaolinite, which was confirmed by the lower $\text{Ca}(\text{OH})_2$ consumption in the modified Chappelle test, higher $[\text{CaO}]$ and $[\text{OH}]$ in the Frattini test and weaker compressive strength.

WPLYW KRystaliczności KAOLINITU I WARUNKÓW KALCYNACJI NA AKTYWNOŚĆ PUCOLANOWĄ METAKAOLINU

Słowa kluczowe

kaolin, krystaliczność, warunki kalcynacji, aktywność pucolanowa

Streszczenie

Do zbadania wpływu krystaliczności i warunków kalcynacji na aktywność pucolanową metakaolinu po dehydroksylacji wybrano dwie rudy kaolinitu o prawie takiej samej jakości i czystości jak oryginalny kaolinit, ale o różnej krystaliczności kaolinitu (indeks Hinckleya). Przeprowadzono różne warunki kalcynacji, zmieniając temperaturę kalcynacji i czas przetrzymywania w celu uzyskania różnych próbek metakaolinu o różnych stopniach dehydroksylacji. Następnie zbadano aktywność pucolanową próbek metakaolinu za pomocą zmodyfikowanego testu Chappelle'a, testu Frattiniego i oceny wytrzymałości. Ponadto obliczono pozorne energie aktywacji dwóch rud kaolinitu w celu zbadania właściwości termicznych kaolinitu metodami izokonwersji, a następnie obliczeń iteracyjnych. Wyniki pokazały, że aktywność pucolanowa była zależna od stopnia dehydroksylacji, z wyjątkiem metakaolinów kalcynowanych w temperaturze 900°C z powodu rekrytalizacji, a wysoką aktywność pucolanową przeprowadzono przez całkowitą dehydroksylację (stopień dehydroksylacji $\geq 90\%$). Ponadto niższa krystaliczność oryginalnego kaolinitu sprzyjała usuwaniu strukturalnych grup hydroksylowych, prowadząc do zmniejszenia pozornej energii aktywacji i wzrostu aktywności pucolanowej, co wskazuje, że wyższa temperatura kalcynacji lub dłuższy czas przebywania były wymagane podczas kalcynacji, aby osiągnąć ten sam stopień dehydroksylacji i wreszcie wysoce uporządkowany kaolinit przekształcony w mniej aktywny metakaolinit, co zostało potwierdzone przez mniejsze zużycie $\text{Ca}(\text{OH})_2$ w zmodyfikowanym teście Chappelle'a, wyższe $[\text{CaO}]$ i $[\text{OH}]$ w teście Frattiniego oraz słabszą wytrzymałość na ściskanie.