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POZZOLANIC PROPERTIES OF FLASH-CALCINED KAOLINITE: A COMPARATIVE STUDY WITH SOAK-CALCINED PRODUCTS.

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ABSTRACT

Flash-calcination enables the dehydroxylation of powdered kaolinite clay within several tenths of a second , when traditional soak-calcinations require minutes at least. The pozzolanic properties of the metakolin produced from two different kaolinites, using two different flash calciners, are shown to increase with the dehydroxylation rate, and rapidly to decrease at the occurence of recrystallisation for temperatures above 900°C. Flash-calcined products also revealed structural properties different from soak-calcined products. Two different lime reactivity tests were thus necessary to asses the pozzolanic properties of products: the compressive strengths of minicylinders of metakaolin+lime+water after solidification, and the Chapelle test. Processing flash-calcination in a temperature range that was determined, with a sufficient residence time, lead to metakaolins with lime reactivities similar or better than reactivities of standard metakaolin obtained by soak-calcination.

Introduction

Flash-calcination processes are being employed in industrial applications with increasing frequency. The minerals sector is particularly interested in this technique; manufacturers of paints, polymers and more recently hydraulic binders consume considerable quantities of calcined kaolinite.

During the calcination of kaolinite, dehydroxylation leads to the metakaolin state (between 500°C and 900°C) according to the reaction $Al_2Si_2O_5(OH)_4 \longrightarrow Al_2O_3 2SiO_2 + 2\ H_2O$. The resulting metakaolin phase offers good properties as a mineral additive. It is X-ray amorphous, and it lends itself particularly well to reaction with lime and therefore makes a good synthetic pozzolana.

Kaolinites are traditionaly calcined in rotary kilns for a matter of hours. The use of fluidised bed processes allows a reduction in time to a matter of minutes (4, 1). After both these types of calcinations, it is necessary to grind the products (that have hardened) to give them the fine granularity needed for their use.

The aim of the present work was to reduce the calcination time to a few seconds, using flash-calcination processes on fine products which will not necessarily be ground after calcining. This can simplify industrial production installations and decrease the energy cost of grinding. Deagglomeration of raw kaolinite indeed requires far less energy than does post-calcination grinding of metakaolin. Flash-calcination consists of a very rapid heating, calcining and cooling of powdered materials which are suspended in a gas.

We have treated two different kaolinites, both in a laboratory flash-calciner, and in an industrial pilot flash-calciner, to manufacture pozzolana. Different qualities are obtained by varying the temperature and time of flash-calcination (500°C to 1000°C, and 0.5 s to 12 s). Results are reported from two different types of lime reactivity measurements of the flash-calcined kaolinites, and a comparison is established with conventional soak-calcined products.

Experiments

Materials

The first kaolinite, denoted K, comes from Morbihan (France). It is a fine laboratory washed powder (91% < 10 µm; 50 % < 2 µm). The second one, denoted KM, was extracted in Montguyon (France), crushed and dried. Pellets were then ground with a ball mill and sieved to 500 µm. Its appearance is therefore coarser (100% < 500 µm; 32 % < 80 µm) than kaolinite K. Differential Thermal Analysis (D.T.A.) of the two kaolinites (in the appendix) show a large endothermic band circa 570°C due to dehydroxylation, and an exothermic band circa 1000°C rendering recrystallisations from the amorphous phase into mullite and cristobalite.

Characteristics of the two clays are given in the appendix.

Calciners

Soak-calcinations were carried out at temperatures ranging from 500°C to 1000°C in an electric furnace. Products were maintained for five hours at a constant temperature and cooled naturally by removing them from the furnace. The two flash-calciners have been described elsewhere (5). Their construction is shown in Figures 1a and 1b. They enabled processing temperatures ranging from 500°C to 1000°C.

The laboratory flash-calciner could only perform calcination of the fine clay K. Residence time was 0.54 seconds.

The pilot flash-calciner of F.C.B. (Lille, France) has enabled trials with residence times of 2, 6 and 12 seconds. Kaolinite K has only been calcined with a two seconds residence time; longer periods induced the loss of too great a quantity of product due to cyclone collecting inefficiency.

Lime reactivity measurements

The first test, carried out with all products, was a measure of compressive strengths of minicylinders of "metakaolin + lime + water". Their diameter was 2 cm and their height 4 cm. The MK/CH ratio (MK = metakaolin; CH = Calcium Hydroxide = lime) was 1.5. A laboratory slaked lime was chosen. It was guaranteed to have 96% $Ca(OH)_2$. Calcined-kaolinite KM was ground and sieved to less than 200 µm prior to minicylinder preparation. Calcines of K were directly used. Pastes were manufactured to the French standard NFP 15-402, gauged in the moulds, removed after 7 days and then stored in water at 20 °C. For each reported value, the compressive strengths of 6 minicylinders were measured at 28 days. We discounted the highest and the lowest values and calculated the average strength.

The second test was a measure of quantity of lime that reacts with metakaolin in the Chapelle test. One gramm of metakaolin was made up into a suspension in distilled

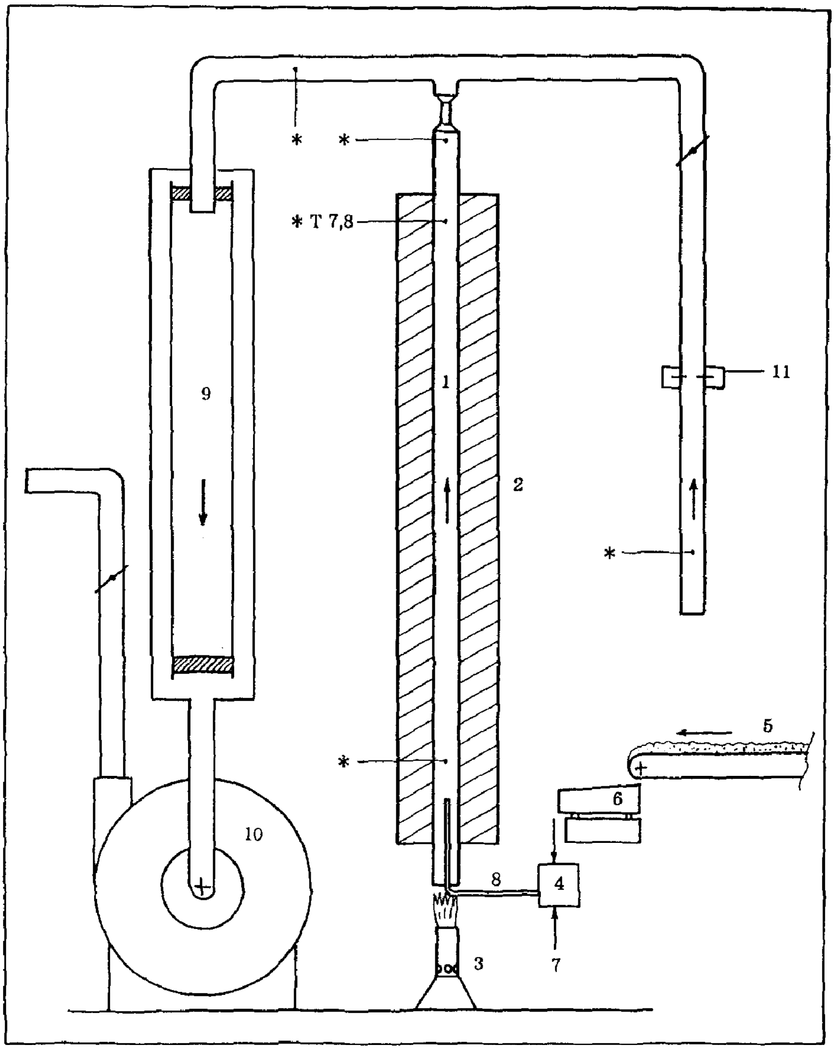

Figure 1a. Construction of the laboratory flash-calciner. (1) 57.1 mm i.d. refractory steel calcining tube; (2) silica/alumina wool insulation; (3) propane burner; (4) clay suspension generator; (5) conveyer belt (1Kg/h); (6) vibrating corridor; (7) compressed air; (8) 6 mm i.d. refractory steel injection tube; (9) calcine collecting filter; (10) exhaust fan; (11) air flow meter; * temperature measurement points.

heated water (100°C) in the presence of 2 gramms of lime, and left for 16 hours. The remaining quantity of lime in the solution is then determined. Results are expressed in gramms of lime reacted per gramm of metakaolin; the precision is ± 5 %.

Results and discussion

Flash-calcinations achieved up to 98 % of the dehydroxylation of clays ($\alpha = 0.98$). Kinetics of these reactions have been studied previously (5) and it has been established that metakaolins have particular mineralogical and rheological properties (8, 2, 3).

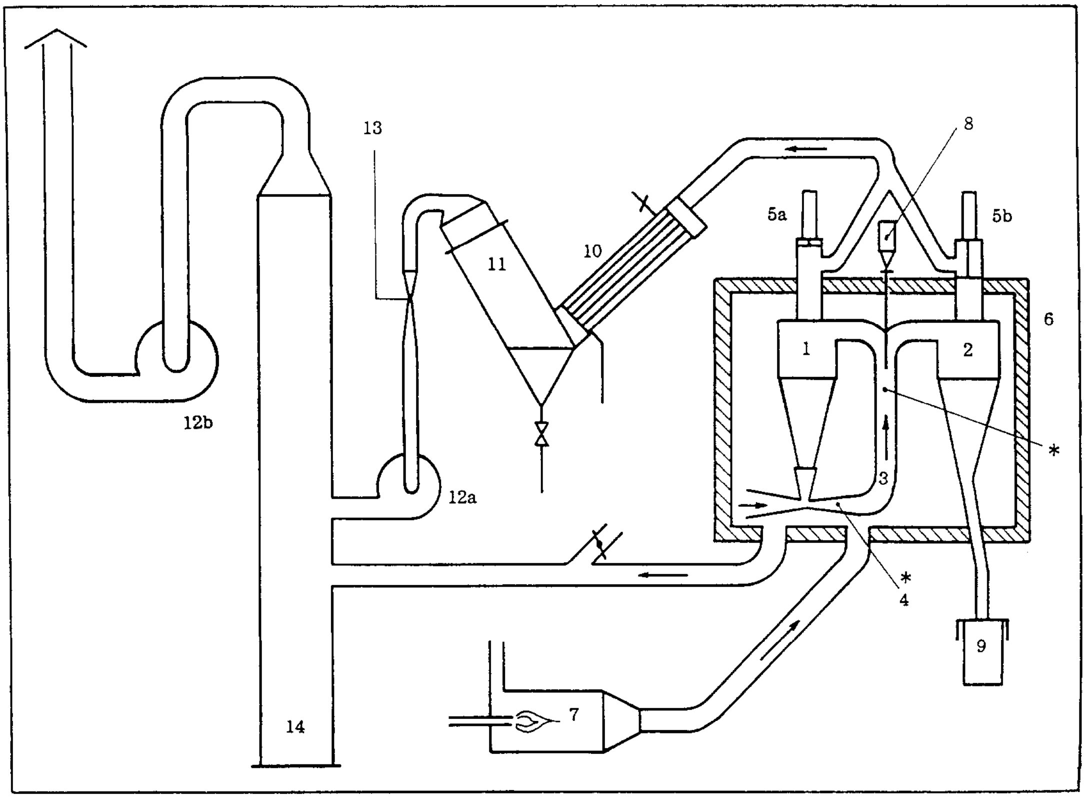

Figure 1b. Construction of the F.C.B. flash-calciner pilot. (1) 300 mm diameter refractory steel exchange cyclone; (2) 300 mm diameter refractory steel exchange cyclone; (3) recycling loop column; (4) injector; (5a, 5b) electro-gates; (6) insulated casing; (7) fuel burner generating hot gas; (8) batch material feed; (9) material collector; (10) gas cooler; (11) air filter; (12) exhaust fans; (13) gas flow meter; (14) air washer; * temperature measurement points.

Kaolinite K

Minicylinders from soak-calcined products were gauged from metakaolin-lime mixtures with a W/S ratio (W = water; S = solid = MK+CH) of 0.75. For the ones which were from flash-calcined metakaolin, we had to use a W/S ratio of 1. In fact, the absorbing properties of these products did not lead to pastes that can be gauged when W/S was 0.75. We gauged one of the soak-calcined products with W/S = 1 to enable a comparison when all parameters are equal. We observe in Figure 2 a clear drop in performance compared with the result for W/S = 0.75. This effect is similar to that obtained by Murat that we also give in Figure 2.

Soak-calcination results (Figure 3) confirm the existence of a temperature range between 550°C and 850°C where the quality of the metakaolin is approximately constant. This has been observed previously (7).

A calcination temperature of 900°C is too high because it induces several recrystallisations from the amorphous phase, and the performance drops rapidly. We characterized the recrystallisation state through measurements of the D.T.A. exothermic band's surface area (height of the band * width of the band at half height); a low band

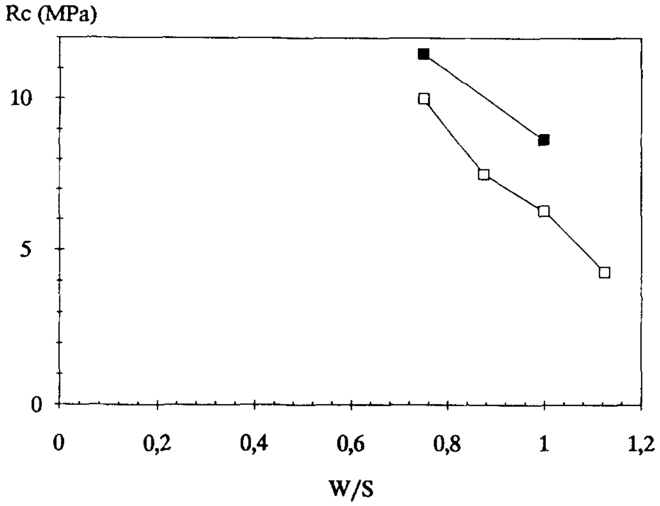

Figure 2. Influence of the W/S ratio (Water/Solid) on compressive strengths at 28 days of minicylinders of "metakaolin+lime+water". (□) Results of Murat; (■) Present results with soak-calcined kaolinite K gauged with W/S=0.75 and W/S=1.

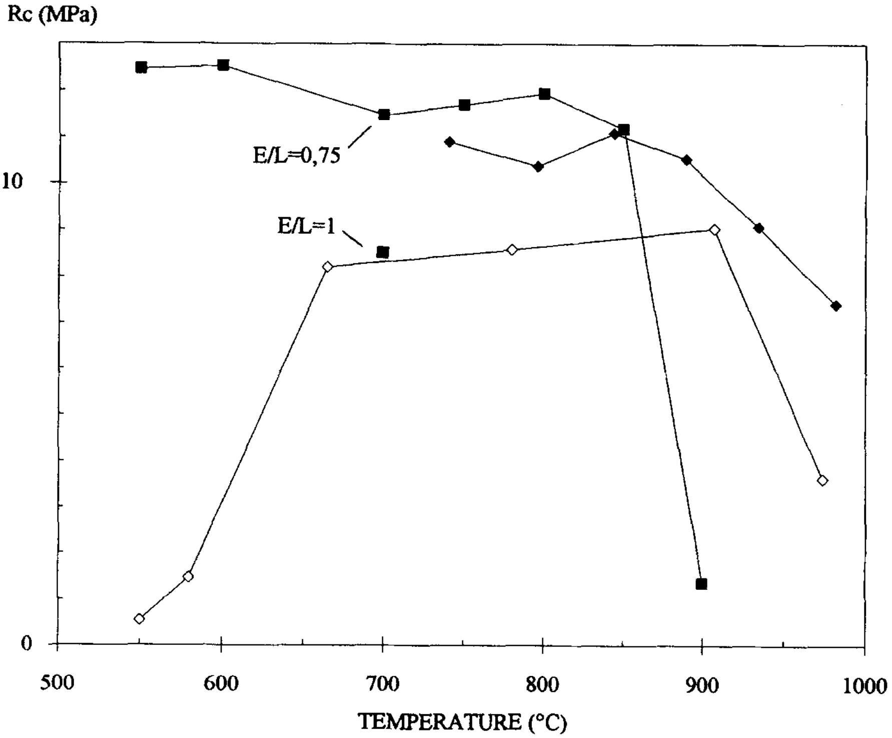

Figure 3. Compressive strengths at 28 days of minicylinders made from kaolinite K calcined at different temperatures. (■) Soak-calcination (E/L = 0.75); (◇) Laboratory flash-calcination (E/L = 1); (◆) F.C.B. pilot flash-calcination (E/L = 1).

surface area indicated an advanced state of recrystallisation. This surface area in fact decreases from 266 mm^2 for the soak-calcined product at 850°C, down to 49 mm^2 for the soak-calcined one at 900°C (Table 1).

Flash-calcined products behave in the same way (Figure 3) since dehydroxylation is in an advanced state (α closed to 1).

Table 1. Results for kaolinite K. T-Calcination temperature; α-Degree of dehydroxylation; S-Exothermic band surface area on D.T.A. trace; σ-Compressive strength at 28 days from test minicylinders MK+CH+W.

Soak-calcinations (5 hours)

T (°C)	550	600	700	750	800	850	900
α	0.87	0.93	0.96	0.96	0.98	0.98	0.98
S (m^2.10^{-6})	-	-	-	-	210	266	49
σ (MPa); W/S = 0.75	12.5	12.5	11.5	11.7	11.9	11.2	1.4
W/S = 1			8.7				

Laboratory flash-calcinations (0.54 seconds)

T (°C)	550	580	665	780	907	974
α	0.15	0.23	0.65	0.80	0.93	0.96
S (m^2.10^{-6})	-	-	-	179	119	65
σ (MPa); W/S=1	0.54	1.5	8.2	8.6	9.0	3.6

F.C.B. flash-calcination (2 seconds)

T (°C)	740	796	844	889	934	982
α	0.91	0.93	0.96	0.97	0.96	0.97
S (m^2.10^{-6})	-	-	-	259	152	132
σ (MPa); W/S=1	10.9	10.4	11.1	10.5	9.1	7.4

Laboratory flash-calcinations have induced recrystallisation during trials at the highest temperatures. Recrystallisations have also been estimated through exothermic band surface areas on D.T.A. plots; the latter decrease with the binder's performance (Table 1). The calcination time of 0.54 seconds is too short to achieve total dehydroxylation of clay without generating recrystallisation, and the binding performances are mediocre.

A 2 seconds-calcination in the F.C.B. pilot, however, enables both the conditions of total dehydroxylation and the lack of recrystallisations to be fulfilled, and high binding strengths are obtained. A drop in performance also occurs at the highest temperatures which shows a good correlation with the reduction of the exothermic band's surface area on D.T.A. (Table 1).

Kaolinite KM

It was possible to gauge all products, soak- or flash-calcined, with a W/S ratio of 0.75.

A temperature of at least 600°C must be used during a 5 h soak-calcination to obtain a good metakaolin (α = 0.89), as shown in Figure 4. Above that temperature and up

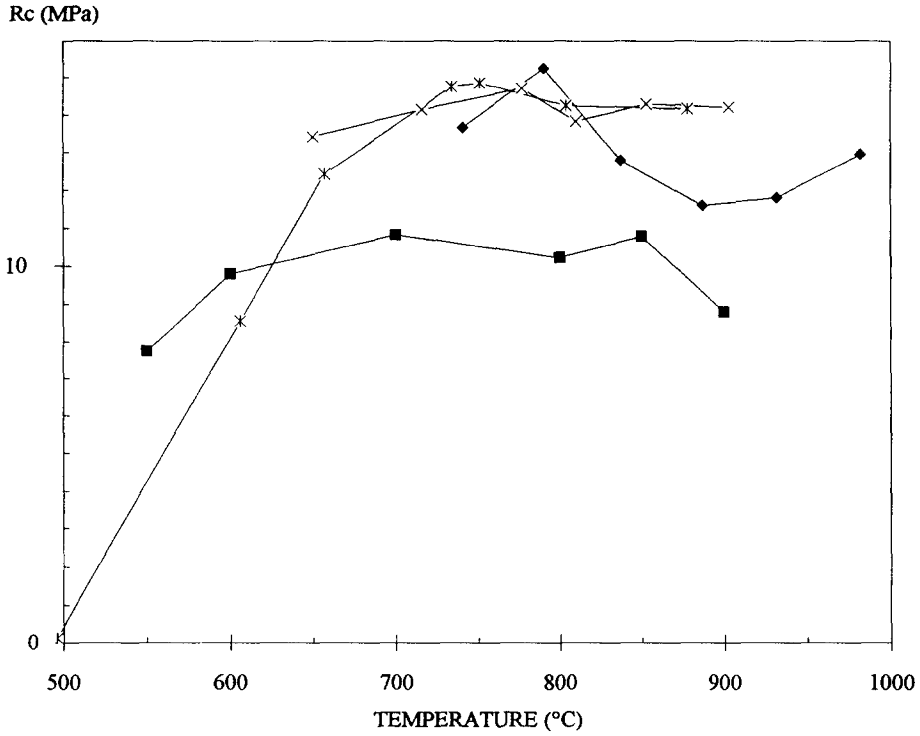

Figure 4. Compressive strengths at 28 days of minicylinders made from kaolinite KM calcined at different temperatures. (■) Soak-calcination (E/L=1); F.C.B. pilot flash-calcination (◆) 2 seconds, (✱) 6 seconds, (×) 12 seconds (E/L=1).

to 850°C, the pozzolana quality remains approximately constant, as is the case with kaolinite K. At 900°C, the strength drops; minicylinders made with KM calcined at 950°C had not even solidified after 7 days. Recrystallisations are always the cause of this drop; we have again quantified this transformation in Table 2, which indicates a correlation between the performance of the binder and the surface area of the exothermic band on D.T.A. traces.

The series of calcines produced after 6 s on the F.C.B. pilot shows proportionality of mechanical strengths and α (Table 2) when products are only partialy dehydroxylated (4 points at lowest temperatures). Above that temperature, performance remains constant in the studied domain.

The two other series calcined for 2 s and 12 s indicate that residence time has little influence on the quality of metakaolins, since dehydroxylation is in an advanced state. There is, nevertheless, a slight deterioration in the quality of the series of products calcined for 2 seconds.

Synthesis

Results with kaolinite K indicate equivalent strengths of minicylinders from soak- and flash-calcined products provided that the W/S=1 ratio is conserved. The two calcination modes, soak and flash (when residence time is longer than 0.54 s), allow a temperature range giving well dehydroxylated and non-recrystallised clays which form good metakaolins under the lime reactivity criterion.

Table 2. Results for kaolinite KM. T-Calcination temperature; α-Degree of dehydroxylation; S-Exothermic band surface area on D.T.A. trace; σ-Compressive strength at 28 days from minicylinders MK+CH+W.

Soak-calcinations (5 hours)

T (°C)	550	600	700	800	850	900	950
α	0.68	0.89	0.95	0.97	0.98	0.98	0.98
S ($m^2.10^{-6}$)	-	-	-	-	-	225	#0
σ (MPa); W/S=0.75	7.8	9.8	10.8	10.2	10.8	8.8	#0

F.C.B. flash-calcinations (2 seconds)

T (°C)	741	790	837	887	932	982
α	0.89	0.90	0.94	0.95	0.97	0.97
S ($m^2.10^{-6}$)	-	-	-	-	-	-
σ (MPa); W/S=0.75	13.7	15.3	12.8	11.6	11.8	12.9

F.C.B. flash-calcinations (6 seconds)

T (°C)	496	606	657	734	751	804	878
α	0.12	0.51	0.73	0.88	0.90	0.94	0.97
S ($m^2.10^{-6}$)	-	-	-	-	-	-	-
σ (MPa); E/L=0.75	0.13	8.6	12.4	14.8	14.9	14.3	14.2

F.C.B. flash-calcinations (12 seconds)

T (°C)	650	716	777	810	853	903
α	0.87	0.94	0.95	0.97	0.98	0.98
S ($m^2.10^{-6}$)	-	-	-	-	-	224
σ (MPa); E/L=0.75	13.4	14.1	14.7	13.8	14.3	14.2

Mechanical strengths of minicylinders made with calcined KM lead to the same observations. Better performances are obtained with flash-calcined products than with traditional products.

There is a degree of uncertainty in the interpretation of previous results on account of "liquidity of pastes MK+CH+W" (or W/S ratio) that largely influences mechanical strengths, and is likely to be changed according to the calcination process used. For this reason, we carried out the Chapelle tests where these considerations do not arise.

Only the best product in each series (of temperature variation) has been studied. Results are given in Figure 5b, and we recall mechanical strengths of minicylinders (Figure 5a, with W/S = 1 for K, and W/S = 0.75 for KM). Chapelle reactivity of flash-calcined kaolinite K is slightly lower than for soak-calcined metakaolin. This contradicts results from mechanical strengths. We explain this difference by the fact that the flash-calcined metakaolin has been given an advantage during mechanical strength tests by its high water retention capacity arising during minicylinders manufacture. The soak-calcined product gauged with with W/S = 1 indeed gave a very liquid paste, which counted against it.

The rougher kaolinite KM did not induce such paste rheology changes, and all pastes from these products were gauged with W/S = 0.75 and had approximately the same

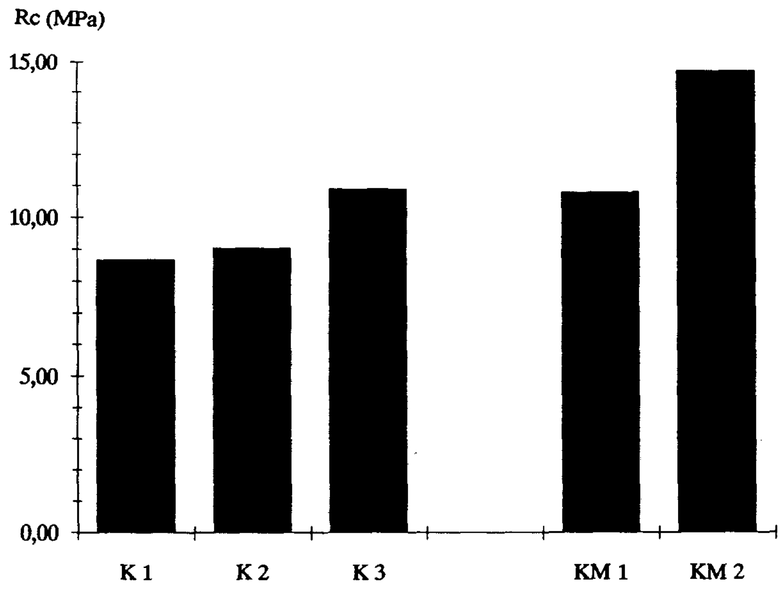

Figure 5a. Compressive strengths, at 28 days, of minicylinders from the best products calcined in the three different calciners; W/S = 1 for K and W/S = 0.75 for KM.

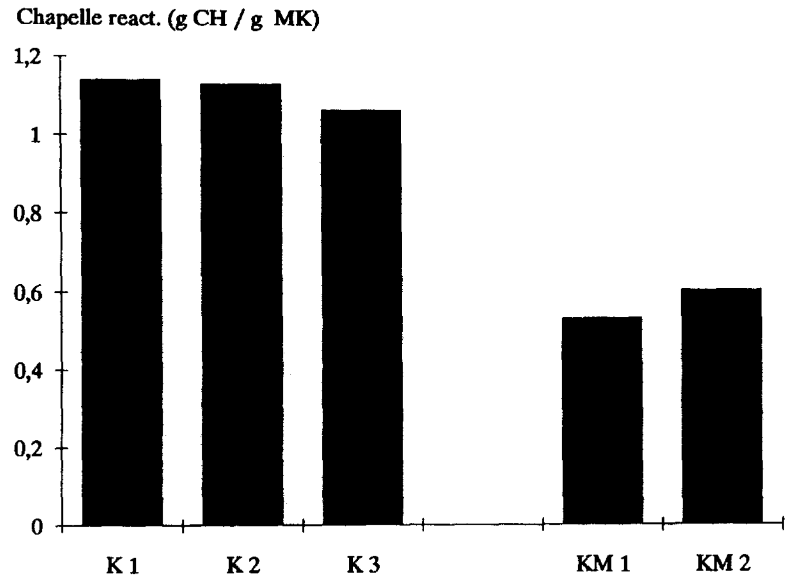

Figure 5b. Chapelle reactivity of the best products calcined in the three different calciners. K1 = Soak-calcined kaolinite K (700°C-5h); K2 = Laboratory flash-calcined kaolinite K (907°C-0.54s); K3 = F.C.B. pilot flash-calcined kaolinite K (740°C-2s). KM1 = Soak-calcined kaolinite KM (700°C-5h); KM2 = F.C.B. pilot flash-calcined kaolinite KM (777°C-12s).

consistency. Under these conditions, indications from the two lime reactivity tests agree: the flash-calcined product is slightly more pozzolanic than the soak-calcined one.

Furthermore, we can note a Chapelle reactivity of KM considerably lower than that of K, when the mechanical strengths of minicylinders from the two clays are comparable. The quality of strengthening is linked with the nature of hydrated minerals that form; they are the same for the two metakaolins. Chapelle reactivity is additionally linked to the reaction surface that the pozzolana presents to the lime. KM is rougher (d_{50} = 160 µm) than K (d_{50} = 2 µm) and therefore presents less reaction surface. This explains why we observed a low Chapelle reactivity for KM.

Conclusion

Flash-calcined thin kaolins present high water absorption capacities, and thus require more water to gauge pastes or mortars. This makes comparison of mechanical strengths with soak-calcined products difficult, which makes it desirable to confirm them by Chapelle tests.

By measuring compressive strengths of minicylinders we were able to verify that, after a flash-calcination, the quality of the pozzolana increases with α values. There is a temperature range from 650 to 900°C in which fully dehydroxylated metakaolins have very similar lime reactivity. Extending calcination time of these metakaolins does not noticeably improve their pozzolanicity.

During the few seconds or tenths of seconds of flash-calcination, temperatures above 950°C induce recrystallisations from the amorphous phase. Recrystallisations are accompanied, as with a soak-calcination, by a rapid drop of lime reactivity. This performance drop is correlated with the decrease of the exothermic band surface area on D.T.A. traces.

Both lime reactivity tests indicate that flash-calcination can manufacture, within a few seconds, metakaolins whose lime reactivity is similar to or better than the reactivity of standard metakaolins obtained by soak-calcination.

Other special properties of flash-calcined kaolinites, such as low density and high light absorption capacity, also add to the attractions of this low specific energy consumption process for the production of metakaolin.

Acknowledgments

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Appendix

Characteristics of kaolinites

	K	KM
Specific surface (m^2/g)	13.4	11.2
Density	2.59	2.58
Loss on ignition (NFP 15-461)	12.0 %	11.6 %

Chemical analysis of kaolinite K

SiO_2 = 47.53 %
Al_2O_3 = 36.75 %
K_2O = 1.45 %
Fe_2O_3 = 0.79 %

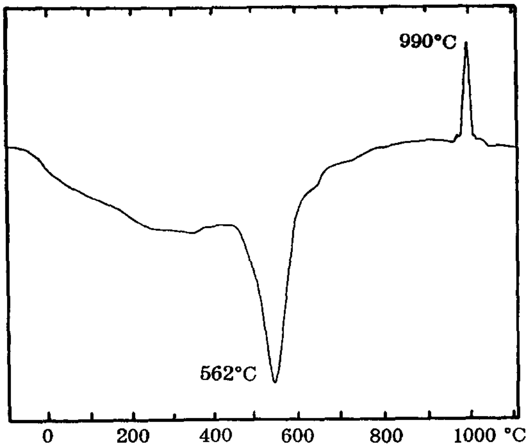
P_2O_5 = 0.11 %
TiO_2 = 0.10 %
MgO = 0.2 %
L.O.I. = 12.89 %
Total = 99.82 %

Chemical analysis of kaolinite KM

SiO_2 = 49.03 %
Al_2O_3 = 34.20 %
K_2O = 0.78 %
Fe_2O_3 = 1.20 %
CaO = 0.07 %

P_2O_5 = 0.07 %
TiO_2 = 1.60 %
MgO = 0.11 %
L.O.I. = 12.69 %
Total = 99.77 %.

Differential Thermal Analysis of kaolinite K



Differential Thermal Analysis of kaolinite KM