Development of Highly Reactive Metakaolin from Paper Sludge

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The paper industry in Western Europe generates around 6 million tons/year of sludges, which contain about 60% dry matter mainly composed of cellulose fibers, kaolinite, and calcite. The present study deals with an original way of utilizing such wastes: the production of metakaolin by calcining paper sludge in the temperature range of 700°C to 800°C. After calcination, pastes containing 50% calcium hydroxide and 50% burnt sludge were hydrated and the lime consumption investigated by differential thermal analysis. The results show that a very reactive pozzolan is produced by calcining paper sludge at 700°C or 750°C for 2 or 5 hours. Despite a smaller kaolinite content, the burnt paper sludge exhibits more pozzolanic activity than commercially available metakaolins, especially at early ages. Thermodesorption analyses show that this higher activity is due to the presence of superficial defects that occur during the sludge calcination. ADVANCED CEMENT BASED MATERIALS 1998, 7, 49–56. *© 1998 Elsevier Science Ltd.*

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In densely populated industrial countries, regulations to protect the environment and the potential risk to groundwater quality have led in recent years to a drastic reduction in the amount of available landfill space and a huge rise in the cost of land disposal of waste. Prevention and recycling of wastes is being encouraged by political authorities.

Processing of waste paper generates fiber residues and sorting wastes (de-inking and waste water-treatment sludges). Until now, this paper residue was disposed of mainly by landfilling, discharge for agricultural purposes, composting, and utilization in the brick-making industry [1]. In recent years, the paper industry has also been trying to dispose of the paper residue by thermal means in its own, very expensive, incinerators. Here, the biggest problem is disposal of the resulting ash, which often makes up 25% of the volume of the paper residue.

The Wopfing Cement Works in Austria [2] developed a new technology for 50,000 tons/year fiber residue processing in a cement kiln. This technology utilizes the calorific value of the dried paper fibers and the fiber residue ash, which contains limestone, and clay is used as raw material for the production of cement clinker.

In the present study, an original method of utilization is proposed: the production of a very reactive pozzolan by a controlled-calcination process. The composition of the mineral fraction of the paper sludge is suitable for such production; it is composed mainly of highly pure kaolin and natural limestone. The temperature of calcination is chosen in the range of 700°C to 800°C to destroy the combustible cellulose fibers present in the waste and prevent the decarbonation of limestone. The pozzolanic activity of the calcined sludge is studied through the calcium hydroxide consumption in calcium hydroxide-sludge mixtures and compared to that of commercial metakaolin issued from the calcination of natural clays. The results show that it is possible to transform paper sludge to a highly reactive metakaolin that can be used in the concrete industry.

Description of Paper Sludges

Two paper sludges were investigated: a de-inking sludge, D, and a waste water-treatment sludge, W. Their dry matter content was around 60%. The chemical analysis of the dry matter is reported in Table 1.

X-ray diffraction (XRD) analyses of dried sludges are presented in Figures 1 and 2. They show that the main components of the inorganic fraction are calcite, kaolinite, muscovite, quartz, and talc.

A quantitative approach to the mineralogy of sludges was conducted, according to the following assumptions:

- all the organic carbon is considered as cellulose, $C_{12}H_{20}O_{10}$,
- calcium is mobilized by calcite, $CaCO_3$,
- potassium is only present in muscovite $(Al_2O_3)_3$, $(SiO_2)_6K_2O(H_2O)_2$,
- magnesium is entirely in talc, $Mg_3Si_4O_{10}(OH)_2$,
- aluminum is present both in kaolinite Al_2O_3, 2 SiO_2, 2 H_2O, and muscovite,
- silica is shared between talc, kaolinite, and quartz.

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TABLE 1. Chemical composition of the dry matter contained in the sludges (% by mass)

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	P_2O_5	LOI	Organic Carbon
D	21.9	11.2	0.8	14.3	4.1	0.4	0.2	0.2	0.1	46.0	17.3
W	21.8	16.4	0.8	6.8	1.2	0.2	0.1	0.7	1.2	50.6	16.2

TABLE 2. Mineralogical composition of the dry matter of sludges (% by mass)

Element	Organics	Kaolinite	Talc	Quartz	Muscovite	Calcite	Total
D	38.8	26.3	12.8	0.6	2.0	18.6	99.1
W	39.7	35.8	3.8	0.7	5.8	12.2	98.0

The results are presented in Table 2. Sludge W is richer in kaolinite than sludge D.

Experimental Procedure

Calcination of Sludges

Sludges were burnt in a laboratory electrical fixed-bed furnace. The volume of the furnace was 125 L and the quantity to calcine was 5 kg of wet sludge. Due to the presence of organics and water in the sludge, the calcination occurred under water vapor and carbon dioxide pressures. Previous investigations showed that these conditions could have an influence on the pozzolanic activity of thermally activated clays [3]: the water vapor pressure modifies the surface properties of calcined montmorillonites leading to a slight decrease of the reactivity at early ages; however, the pozzolanic activity at 28 days is not affected.

Three temperatures of calcination were chosen, 700°C, 750°C, and 800°C, to preserve the calcite present in the sludge. The temperature rate was 250°C/hour. The product was maintained at the desired temperature for 2, 5, or 21 hours. Then it was cooled, with the furnace being closed. The discharging took place as the furnace recovered to ambient conditions. The cooled burnt sludge was milled for 30 minutes to obtain particles less than 100 μm. Laser granulometry and BET surface area analyses were carried out to characterize the physical properties of the final product.

XRD analyses were also done to investigate the dehydroxylation of kaolinite and the preservation of calcite, using CuK_α radiation on a Siemens D500 diffractometer equipped with a graphite monochromator.

Pozzolanic Activity of Calcined Sludges

The pozzolanic activity of calcined sludges was investigated by measuring the consumption of calcium hydroxide with time on pastes composed of 50% calcium hydroxide and 50% calcined sludge, by weight. Pastes were

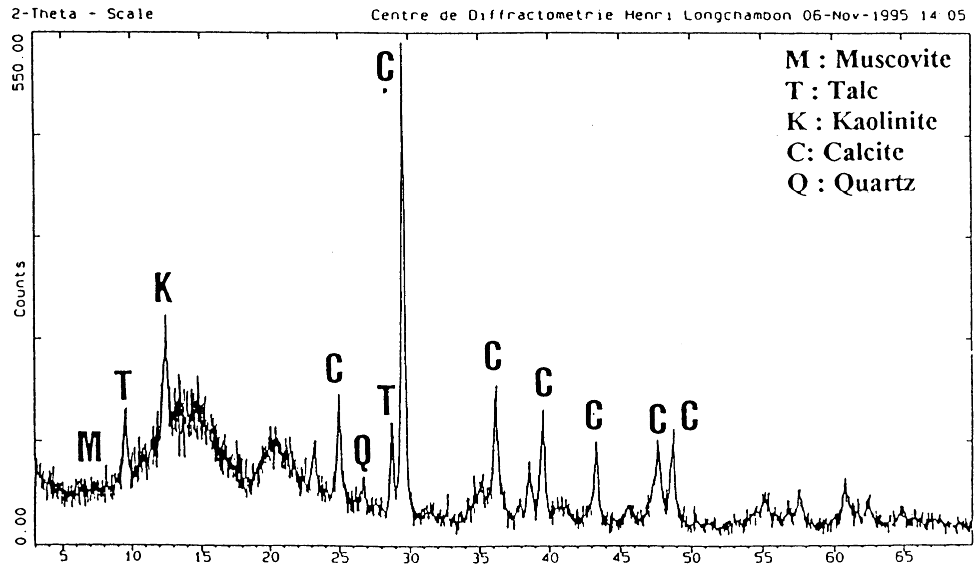

FIGURE 1. XRD analysis of D sludge.

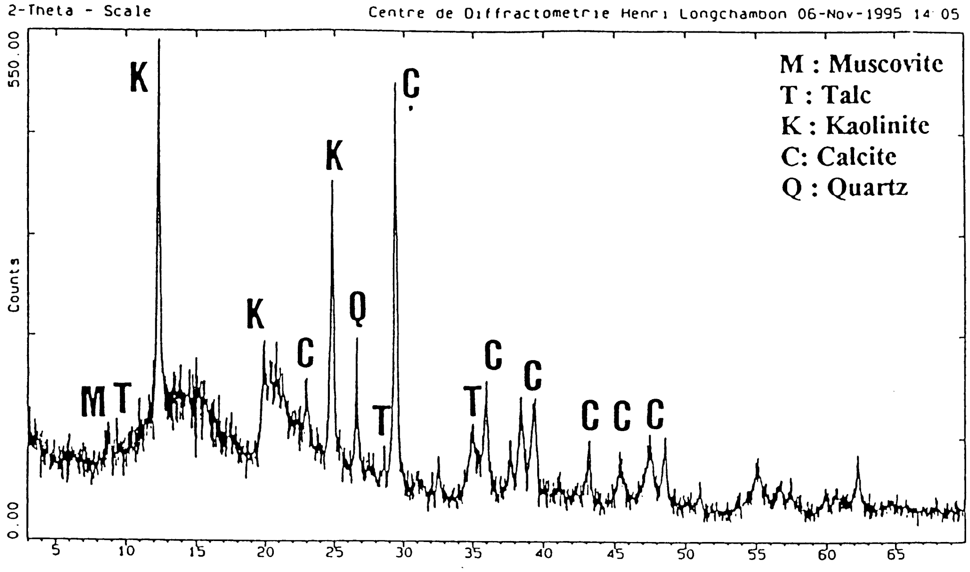

FIGURE 2. XRD analysis of W sludge.

prepared at equivalent consistencies according to the French standard NFP 15-402 and cast into cylindrical molds (diameter: 20 mm; height: 40 mm) using a shaking table. The water to solid ratios are presented in Table 3.

The samples were demolded after 3 days of hydration and immersed in lime-saturated water for 4 or 25 days. Therefore, it was possible to evaluate the calcium hydroxide consumption after 3, 7, and 28 days of hydration. This measurement was done by differential thermal analysis (DTA) on 600 mg of powder less than 100 μm. The surface area of the residual calcium hydroxide peak was measured and compared to that of a paste containing 50% calcium hydroxide and 50% ground silica. The temperature rate was 10°C/min.

The pozzolanic behavior of calcined D and W sludges was compared to that of two commercially available metakaolins: one produced by AGS (France) and the other, by ENGELHARD (USA). These metakaolins are referenced as MKF (AGS) and MKA (ENGELHARD); their properties are given in Table 4.

The water to solid ratios of pastes cast with these metakaolins were 0.61 for MKF and 0.70 for MKA.

Results and Discussion

Characterization of Calcined Sludges

The XRD spectra are shown in Figures 3 to 6. Figure 3 shows that some kaolinite remained after calcining W sludge for 2 hours at 700°C. Kaolinite was completely dehydroxylated when burnt at 700°C for 5 hours. At this temperature, a small decarbonation of calcite appeared after 5 hours of calcination. When W sludge was burnt at 700°C for 21 hours, calcite was almost entirely decarbonated and some anorthite (CaO, Al_2O_3, $2SiO_2$, i.e., CAS_2) was formed. Talc and muscovite were not affected by the calcination. The presence of anorthite, which generally is formed at higher temperatures, can be explained by the fact that the organics present in the sludge ignited and raised the temperature of the matter by 100°C. Traces of well-crystallized anatase also appeared, despite a low content (about 1% in the calcined sludge). Clinochlore [$(Mg, Fe)_6(Si, Al)_4O_{10}(OH)_8$] was present in D sludge calcined at 700°C, but disappeared at higher temperatures. It was not detected in the raw sludge because organics were still present and decreased the quantity of inorganics to be analyzed. The amount of clinochlore was under the limit of detection.

When the temperature reached 750°C, kaolinite was dehydroxylated whatever the length of calcination was, and calcite began to decarbonate after 5 hours of calcination. The same results were obtained at a temperature of 800°C (Figure 4).

As shown in Figures 5 and 6, the same phenomena appeared during the calcination of D sludge:

- total dehydroxylation of kaolinite after a calcination at 700°C for 2 hours,
- decarbonation of calcite as the length of calcination reached 5 hours,

TABLE 3. Water to solid ratios of pastes

Duration of Calcination	2 Hours		5 Hours		21 Hours	
Type of Sludge	D	W	D	W	D	W
Temperature (°C)						
700	0.86	0.83	0.74	0.72	0.73	0.72
750	0.67	0.74	0.71	0.71	0.71	0.68
800	0.73	0.77	0.71	0.75	0.70	0.70

TABLE 4. Properties of metakaolins MKF and MKA

Metakaolin	Mineralogy (%)			Average Particle Size Distribution D_{50} (μm)	BET Surface Area (m^2/g)
	Metakaolinite	Muscovite	Quartz		
MKF	76.5	10.3	8.1	4	18.7
MKA	76.9	0.6	0.0	1	11.9

- formation of gehlenite (2CaO, Al_2O_3, SiO_2, i.e., C_2AS) after 5 hours at 800°C.

In all the calcined samples, the organics were totally destroyed during calcination, as measured by the organic carbon content, which was lower than 0.04%.

Pozzolanic Activity of Calcined Sludges

When only mixed with water, the sludges calcined at 700°C or 750°C for 2 or 5 hours did not set and no strength could be measured. The other products reacted slightly when mixed with water: the lime coming from the decarbonation of calcite reacted with metakaolinite. In this case, the calcined sludges presented hydraulic properties.

The quantity of calcium hydroxide consumed by the pozzolanic reaction is given in Table 5. From the test results, it can be concluded that the conditions of calcination leading to the more reactive pozzolans are 700°C or 750°C for 2 or 5 hours for both D and W sludges. However, calcined W sludge is more pozzolanic than D sludge, which can be explained by a higher kaolinite content.

Table 5 also shows that calcination for 21 hours gives a poorly reactive product, especially at early ages. The reduced lime consumption after 21 hours of calcination is probably due to decomposition of $CaCO_3$ to either CaO or lime-containing compounds (e.g., anorthite and gehlenite) tying up reactive silica. The pozzolanic activity of calcined sludges decreases as the temperature reaches 800°C and the length of calcination 5 hours. This is due to the decarbonation of calcite, which produces excess lime that does not react with metakaolinite. Alumina and silica are also consumed to form inert products such as gehlenite and anorthite, and less metakaolinite is available for the pozzolanic reaction.

The DTA curves (Figure 7) show that the main products of hydration are:

- C-S-H, endothermic peak at 130°C,
- $C_4A\bar{C}H_{11}$, monocarboaluminate, peak at 220°C,
- CH, calcium hydroxide, peak at 560°C.

In Figure 7, it can also be seen that the peak corresponding to calcium carbonate (peak at 870°C) decreases with time. As previously shown by Ambroise [4], the calcium carbonate ($C\bar{C}$) present in the sludge and which is preserved during calcination reacts with lime (CH) and metakaolin (AS_2, i.e., Al_2O_3, 2 SiO_2) according to the following equation:

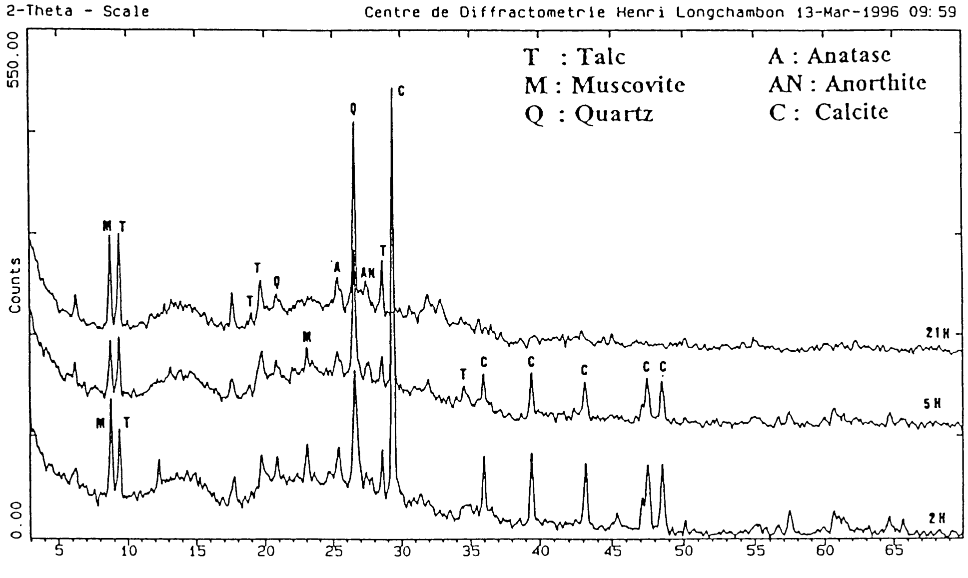

FIGURE 3. XRD spectra of W sludge calcined at 700°C.

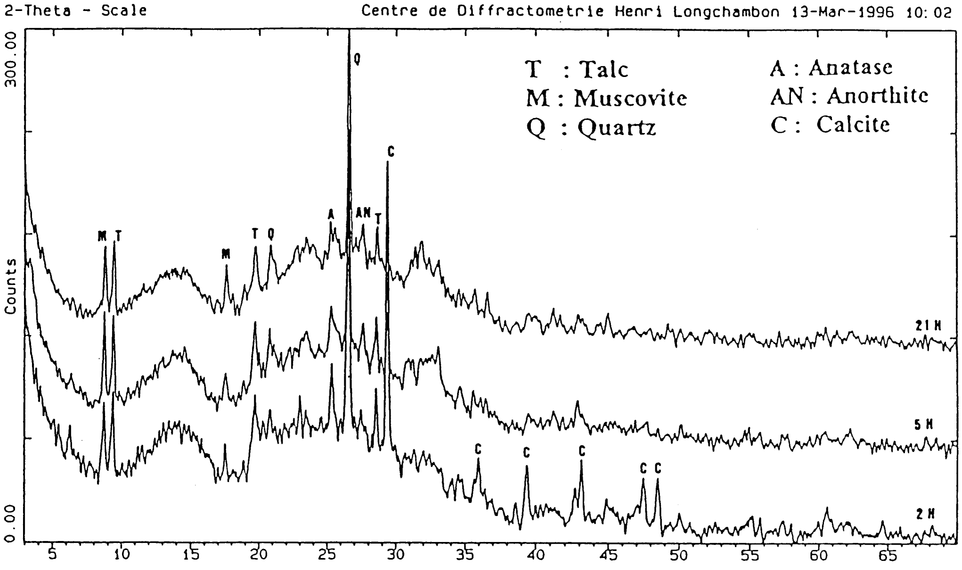

FIGURE 4. XRD spectra of W sludge calcined at 800°C.

$$AS_2 + 5CH + C\bar{C} + 8H \rightarrow C_4A\bar{C}H_{11} + 2C\text{-}S\text{-}H,$$

leading to the precipitation of C-S-H and monocarboaluminate.

The presence of $C_4A\bar{C}H_{11}$ was also detected by XRD (rays at $2\theta = 11.7°$ and $2\theta = 23.5°$).

Comparison with Commercially Available Metakaolins

The reactivity of D and W sludges calcined at 700°C for 5 hours was compared to that of metakaolins MKF and MKA. The results are presented in Table 6, as are the main physical and mineralogical properties of the different products.

The results reported in Table 6 show that:

- calcined D sludge, which presents the "worst" intrinsic properties (low metakaolinite content and BET specific surface area), consumes as much calcium hydroxide as metakaolin MKF, with a better rate of consumption,
- calcined W sludge performs better than the purest metakaolin (MKA), despite a very coarse particle size distribution, mainly due to the agglomeration that occurs during calcination,
- the rate of lime consumption is higher with calcined sludges,
- the metakaolinite content, BET surface area, and

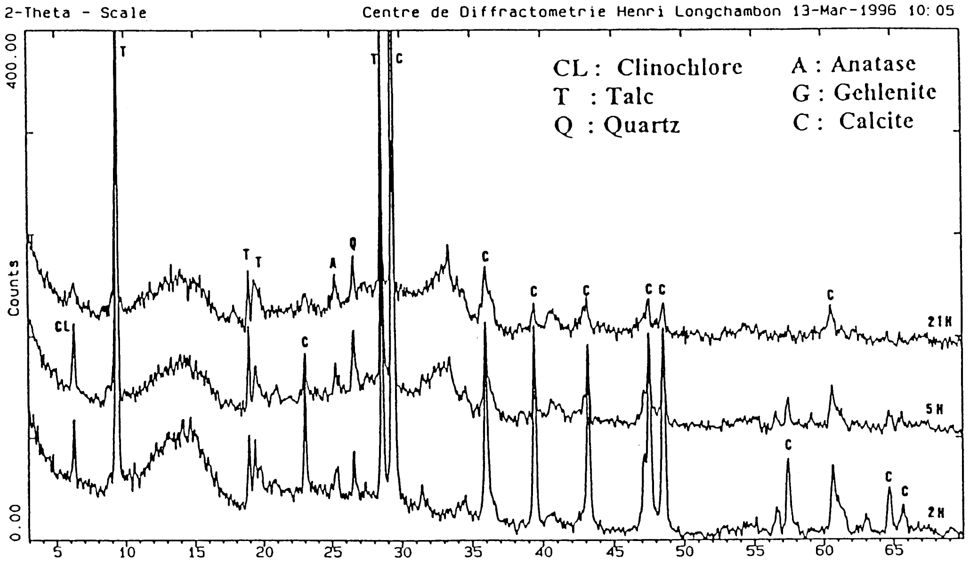

FIGURE 5. XRD spectra of D sludge calcined at 700°C.

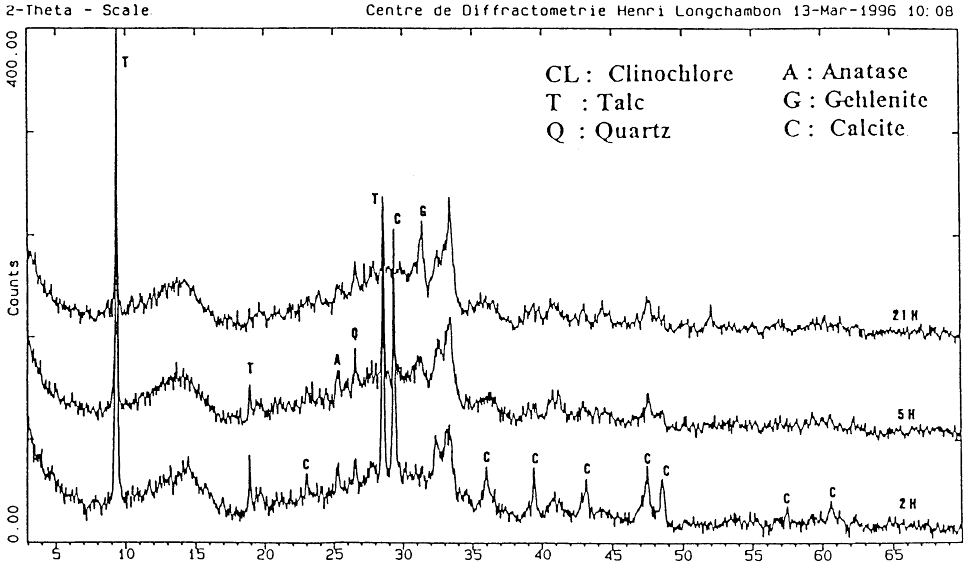

FIGURE 6. XRD spectra of D sludge calcined at 800°C.

particle size distribution are not sufficient to explain entirely the high pozzolanic activity of calcined sludges.

- the better consumption of calcium hydroxide by calcined sludges also can be explained by the formation of the carboaluminate phase, which will not occur in MKF and MKA.

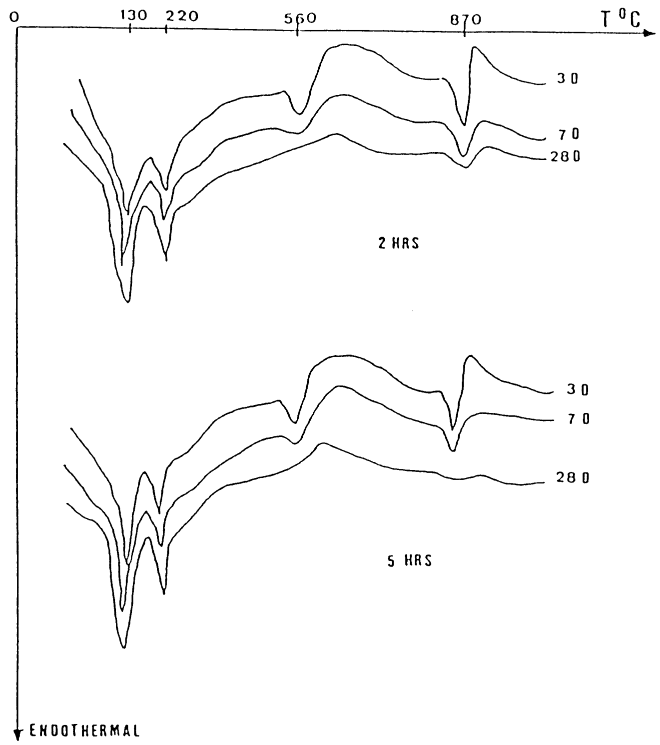

FIGURE 7. DTA curves of hydrated mixtures (50% lime + 50% calcined sludge). Calcination at 700°C for 2 and 5 hours.

According to previous works carried out on calcined clays [3,5], superficial and volumic defects may occur during calcination and increase the pozzolanic activity, especially at early ages. Superficial defects are adsorption sites that are able to adsorb different molecules of gases or liquids. Volumic defects are linked to the porosity of the solid or the presence of hydrates.

Thermodesorption is a technique used to detect the presence of such defects but, in any case, it cannot determine the exact nature of the defect. In this technique, the nature and amount of gas are measured as a function of temperature, while the substance is subjected to a controlled temperature program. The nature of gas is given by the temperature at which the evolved gas is detected and its amount by the surface area of the recorded peak. Thermodesorption is a quantitative analysis and has been utilized to understand the behavior of calcined sludges in comparison with that of metakaolins.

TABLE 5. Calcium hydroxide consumption in mixtures containing 50% calcium hydroxide and 50% calcined sludge

Temperature of Calcination (°C)	Length of Calcination (hours)	Lime Consumption (%)					
		D Sludge			W Sludge		
		3 d	7 d	28 d	3 d	7 d	28 d
700	2	54	73	93	67	95	100
	5	62	65	84	67	92	100
	21	51	64	71	35	36	84
750	2	23	80	90	47	95	100
	5	55	73	75	50	92	100
	21	35	70	72	18	61	84
800	2	57	70	72	39	71	95
	5	38	51	67	27	46	83
	21	18	36	60	27	40	73

TABLE 6. Comparison between calcined D and W sludges (700°C, 5 hours) and metakaolins MKF and MKA

Pozzolan	BET Surface Area (m^2/g)	Average Particle Size D_{50} (μm)	Metakaolinite Content (%)	Calcium Hydroxide Consumption (%)		
				3 d	7 d	28 d
Calcined D sludge	8.4	8	43.6	62	65	84
Calcined W sludge	15.9	29	61.4	67	92	100
MKF	18.7	4	76.5	6	34	80
MKA	11.9	1	96.9	24	45	94

The analyses were conducted between 20°C and 1000°C on 35 mg of product, at a temperature rate of 20°C/min. All masses between 1 and 80 were investigated and the responses obtained only concerned H_2O and CO_2. No CO_2 was found for metakaolins MKF and MKA; it was only present in calcined sludges, due to the presence of calcite. As seen in Figure 8, the behavior of the four products is quite different toward the adsorption of H_2O:

- metakaolins MKF and MKA have about the same behavior, with a strong peak observed between 100°C and 250°C;
- in metakaolin MKF, the peak present between 700°C and 800°C is due to the dehydroxylation of muscovite;
- in calcined W sludge, which is the more reactive product, a strong peak appears between 100°C and 200°C, due to the evolving of adsorbed water;
- in calcined D sludge, the peak between 100°C and 200°C is smaller but has a higher intensity than MKF and MKA. A strong peak appears at over 900°C due to the dehydroxylation of talc.

This water is coming from the water vapor contained in air and which is adsorbed by the calcined product.

The surface area of each peak is proportional to the quantity of adsorbed water. As can be seen from Table 7, this surface area is not proportional to the BET surface area of the product; therefore, the high water loss above 100°C observed in calcined sludges cannot be assigned to the microporosity of these materials. Some superficial defects appeared during calcination.

These effects are slightly the same in D and W calcined sludges because the surface areas of H_2O peaks are proportional to the BET surface areas of these sludges. In this case, the BET surface area and the metakaolinite content are the main parameters having an influence on the pozzolanic activity of the calcined sludges.

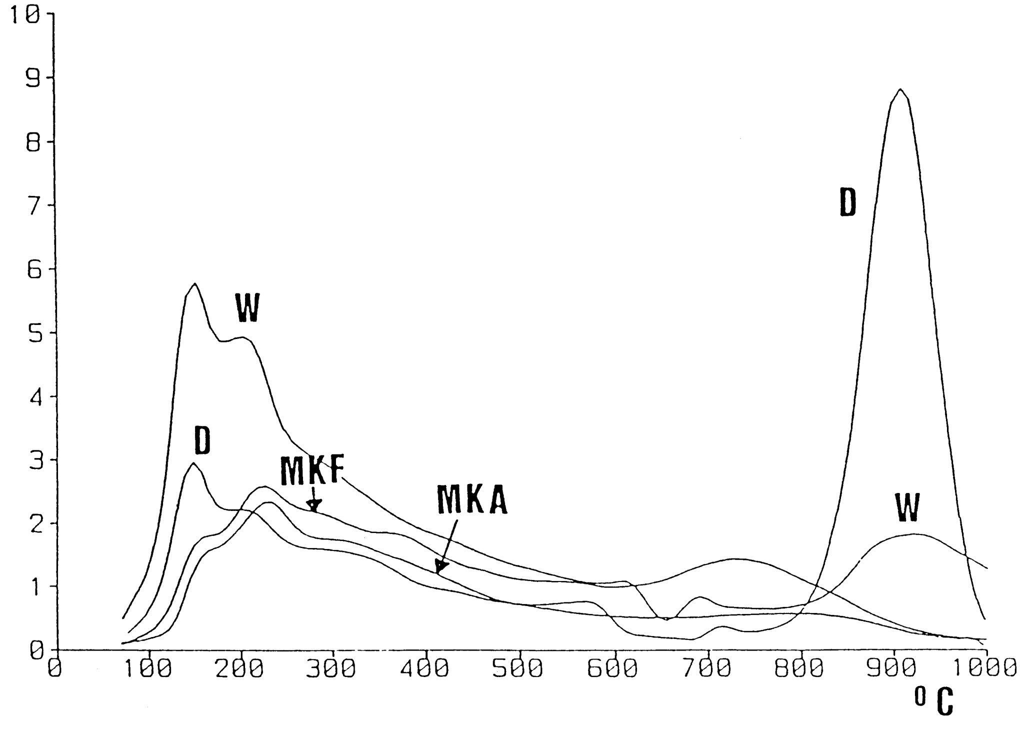

FIGURE 8. Results of thermodesorption tests.

TABLE 7. Surface areas of H_2O peaks and BET surface areas

Pozzolan	BET Surface Area (m^2/g)	Surface Areas of H_2O Peaks (a.u.)	
		164°C	218°C
Calcined D sludge	8.4	1.50	1.34
Calcined W sludge	15.9	3.10	2.96
MKF	18.7	0.98	1.90
MKA	11.9	0.69	1.65

Conclusion

Highly reactive metakaolin can be produced from paper sludge by calcining this waste at 700°C or 750°C for 2 or 5 hours. Superficial defects occur during calcination and increase the reactivity of the burnt product, especially at early ages.

The calcination has to be controlled to entirely destroy the organics present in the sludge and prevent the decarbonation of calcite. Under such conditions, calcite reacts with lime and metakaolin to produce monocarboaluminate and C-S-H.

The proposed process seems to provide an application for paper sludges, avoiding landfilling that has become a very expensive operation in Western Europe. Pilot scale and industrial tests of calcination are being performed, and the production of low cost metakaolin can be expected within a few years. An investigation also has been undertaken to examine the influence of variations in the composition of sludges on their pozzolanic activity. The effect of the material in cement based systems will be presented in a future paper.

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