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RESEARCH ARTICLE

CARACTERISATION OF THE KAOLINITE CLAY MINERALS (NADOR-NORTH MOROCCO) USING INFRARED SPECTROSCOPY AND CALORIMETRY OF DISSOLUTION

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ABSTRACT

The enthalpies of dissolution in hydrofluoric acid of metakaolinites, obtained by thermal dehydroxylation of kaolinite (NADOR-MOROCCO) in the temperature range 450-950°C, have been measured calorimetrically. They are minimum dehydroxylation at 720-800°C. The optimal calcinations parameters, for which complete dehydroxylation of the material, are temperature 650 °C and heating time of 6 H. The conversion of the kaolinite to metakaolinite was confirmed by IR analyses of the starting and thermally treated kaolin samples. The result confirms previous observations about obtaining metakaolinite with optimum reactivity when hydrated with calcium hydroxide as chemical activator.

INTRODUCTION

Development of construction materials which offers technical and environmental benefits is the main challenge of the new millennium. One of such materials is metakaolin (MK), pozzolanic addition, which is classifiedas a new generation of supplementary cementitous material. Supplementary cementitious materials (SCMs) are finely ground solid materials that are used to replace part of the clinker in a cement or cement in a concrete mixture. Use of metakaolin in cement-based systems, provides, beside technical (Mitrović *et al*, 2005; Siddique *et al*, 2009), significant environmental benefits (Mitrović *et al*, 2010). Metakaolin is unique in that it is not the by-product of an industrial process nor is it entirely natural;it is derived from a naturally occurring mineral, and is manufactured specifically for cementing applications. Metakaolin is usually produced by thermal treatment, *i.e.*, calcination of kaolin clays within a definite temperature range. Metakaolin, pozzolanic additive, may be obtainedby calcination of kaolin clay. The optimal conditions of the thermal treatment are: calcination temperature of 650 °C and heating time of 90 min (Ilic *et al*, 2010).

During a thermal treatment in air, the clay minerals are the subject of a number of successive structural transformations involving the dehydroxylation of the solid, then the formation of phases which are being called high-temperature phases (Lawrence *et al*, 2013). Some clays lead by dehydroxylation at intermediate or transitional phases with very marked state of disorganization of the crystal lattice. This phenomenon concerns in particular the kaolinite and halloysite, antigorite and chrysotyle, the montmorillonite, talc, chlorites and some vermiculte (Lemaitre *et al*, 1982). These phases crystallographically disorganized structure generally have a high chemical reactivity and in particular they exhibit a certain pozzolanic pouvoir (consolidation and curing after mixing with water and the calcium hydroxide acting as a chemical activator).

The semi-quantitative analysis of the state of disorganization of the crystal lattice of intermediate phases and of natural and artificial pozzolan can appeal to many experimental techniques including X-ray diffraction (Murat *et al*, 1992), absorption spectroscopy infrared (Frost *et al*, 1996), or for reactivity tests such as monitoring the binding kinetics of the aqueous medium of calcium hydroxide (Murat *et al*, 1988), conductivity (Murat *et al*, 1984) or calorimetry (Mathurin *et al*, 1987).

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The latter method (Mathurin *et al*, 1986) has been used to determine pozzolanic activity of different solids, including the metakaolinite, by studying the evolution of dissolution heat when dissolved in a mixture of hydrofluoric acid and nitric acid and determining the insoluble residue.

We have used this calorimetric method to try to characterize the amorphization state of the metakaolinite by measuring the enthalpy of dissolution in hydrofluoric acid and thus a correlate this data and pozzolanic activity shown of solid according to its temperature dehydroxylation. In this work, the influence of thermal treatment on the structure of Nador-kaolinite (North of Morocco) was studied, using Infrared spectroscopy and dissolution calorimetry.

Experimental

Solution Calorimeter

The 1455 Solution Calorimeter is used for to measure the heat evolved or absorbed by chemical reactions in a liquid media. Measurements are made at room temperature and atmospheric pressure. At the start of a test in this calorimeter, one liquid is held in a glass Dewar while, the other reactant, solid, is held in a Teflon rotating cell sealed which is immersed in the first liquid. After both reactants come to thermal equilibrium, the operator starts the reaction by depressing a push rod to drop the contents of the cell into the surrounding liquid. The reaction then proceeds to completion under the vigorous stirring action of the rotating cell. Throughout the test, temperatures in the calorimeter are sensed by a thermistor and read from a microprocessor based thermometer which is built into the calorimeter case. Digital readings are shown on an LED display and fed to outputs for printer or computer. There is also an analog output for a strip chart recorder to produce a thermogram showing the temperature change produced by the reaction. Data from the thermogram or computer memory can then be used to compute the change in enthalpy.

Table 1 Dissolution tests

concentration of the hydrofluoric acid solution (mol.l^{-1})	Calcinations temperature
7	500°C: End of slow dissolution but exploitable experimental curve 720°C: rapid dissolution 980°C: End of slow dissolution
14.4	Relatively fast dissolution for T < 850°C

The calorimetric technique that we used is clear that if the dissolution is fast enough. Otherwise, the end of the post reaction period is very difficult to determine, and it is virtually impossible to measure the thermal effect correctly (uncertainty can exceed 10% of the value found).
That is why several dissolution tests were initially carried out in different medium to determine the optimum conditions. The nature of the studied aluminosilicate prompted us to choose solutions containing hydrofluoric acid. Following these tests, the solutions were performed in hydrofluoric acid 14.4 mol.l^{-1} obtained by diluting commercial acid (Carlo Erba) to 48% by weight of half. We used a kaolinite Nador in northern Morocco. This kaolinite contains about 1% of quartz, some TiO_2 and ferric ions. In a simplification, the starting kaolinite will be assumed to have only a quartz content of 2%.

Increasing the content of hydrofluoric acid promoted dissolution rate (Table 1), we are directed towards the use of more concentrated of hydrofluoric solutions.

Infrared spectrometry

Spectra were recorded in the range 4000-400 cm^{-1} with a Perkin-Elmer IR 983G spectrophotometer, using samples dispersed in spectroscopically pure KBr pellets.

RESULTS

Calorimetric results

On average, ten dissolutions are carried out on of test portions of 20 to 25 mg for each sample.

The dissolution reaction of metakaolin can be schematically presented in the form:

Al_2O_3, 2 SiO_2, m $H_2O(s)$ + 24 HF(aq) $\longrightarrow$ 2 $H_2SiF_6(aq)$ + 2 $H_3AlF_6(aq)$ + (7+m) $H_2O(aq)$ avec $0 \leq m \leq 2$ (m = 2 for the starting kaolinite).

Upon dissolution, the hydrofluoric acid concentration in the reaction medium thus decreases for two reasons:

1. HF consumption necessary for the formation of H_2SiF_6 and H_3AlF_6
2. Dilution of the solution with both the water formed during the reaction between the acid and the oxides and the residual water in the metakaolin.

Table 2 Enthalpy of dissolution of the metakaolinites

Temp (°C)	m	Molar mass M (g)	lpy of ΔH_{diss} (KJ mol^{-1})	correction $-\Delta H_1 - \Delta H_2$	$[-\Delta H_{diss}]_m$ Corr (KJ mol^{-1})
kaolin	2	263.3	534.44	37.2 + 12.3 = 49.5	484.94
450	0.83	242.4	543.50	36.7 + 12.3 = 49.0	494,50
520	0.31	233.0	599.00	36.53 +12.3 = 48.8	550,20
600	0.15	229.8	672.11	36.45 + 12.3 = 48.7	623.41
700	0.04	228.0	678.90	36.42 + 12.3 = 48.7	630.20
800	0	227.3	671.32	36.42 + 12.3 = 48.7	622,60
920	0	227.3	611.73	36.42 + 12.3 = 48.7	563.00

The comparison of experimental results cannot be done directly for the unit of mass (molar masses of metakaolins are different), we made the necessary corrections to obtain the molar enthalpies of dissolution (based on Al_2O_3). Of the Preceding remarks it is therefore necessary to know the water content for each sample, and to determine the parasitic thermal effect due to the dilution of the acid (Table 2). The molar masses M of the different samples and the corresponding m values are obtained from the weight loss observed at high temperatures until complete dehydration (Table 2). As we noted earlier, we assume that the only impurity in the initial kaolinite is the presence of quartz, hence the general formula:

Al_2O_3, 2 SiO_2, m H_2O + 0.0878 SiO_2 (q)

Thermal effect the HF dilution ΔH_1

The general calculation method (Bousquet *et al,* 1976) to estimate the thermal effects resulting from the dilution of an acid or by acid consumption or by formation of water is used here. For one mole of metakaolin Al_2O_3, 2 SiO_2, m H_2O dissolved in a solution of hydrofluoric acid (HF, x H_2O), the total thermal effect is expressed in the form:

$$\Delta H_1 = h\,(m + 7 + 24x)$$

For x = 3.2 the value of h is:

$$h = \frac{d\left[\Delta H_f^0(HF, xH_2O)_{298}\right]}{dx}$$

This value is equal to -400 $J.mol^{-1}$ (Johnson *et al,* 1973). The overall thermal effect per mole of metakaolin is close to:

$$\Delta H_1 = -400(m + 7 + 24 \times 3.5) = -400(91 + m)\, J.mol^{-1}$$

We can notice that the residual water of metakaolin has a negligible effect because the values of m are always less than 0.85, except for the starting kaolin.

Thermal effect the dissolution of quartz ΔH_2

The dissolution of the quartz in the kaolin is performed according to the reaction:

$$SiO_2\,(q) + 6\,HF\,(aq) \xrightarrow{\qquad} H_2SiF_6\,(aq) + 2\,H_2O\,(aq)$$

The heat of this reaction is of the order of -140 kJ mol^{-1} (Wagman *et al,* 1982), therefore a thermal effect ΔH_2 neighboring of -12.3 kJ per mole of metakaolin.

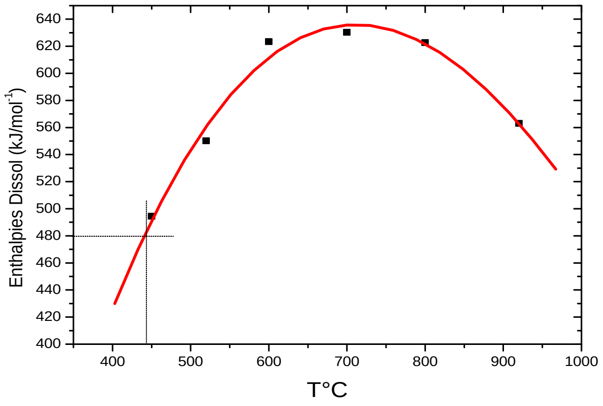

Figure 1 Enthalpy of dissolution in hydrofluoric acid depending on the treatment temperature

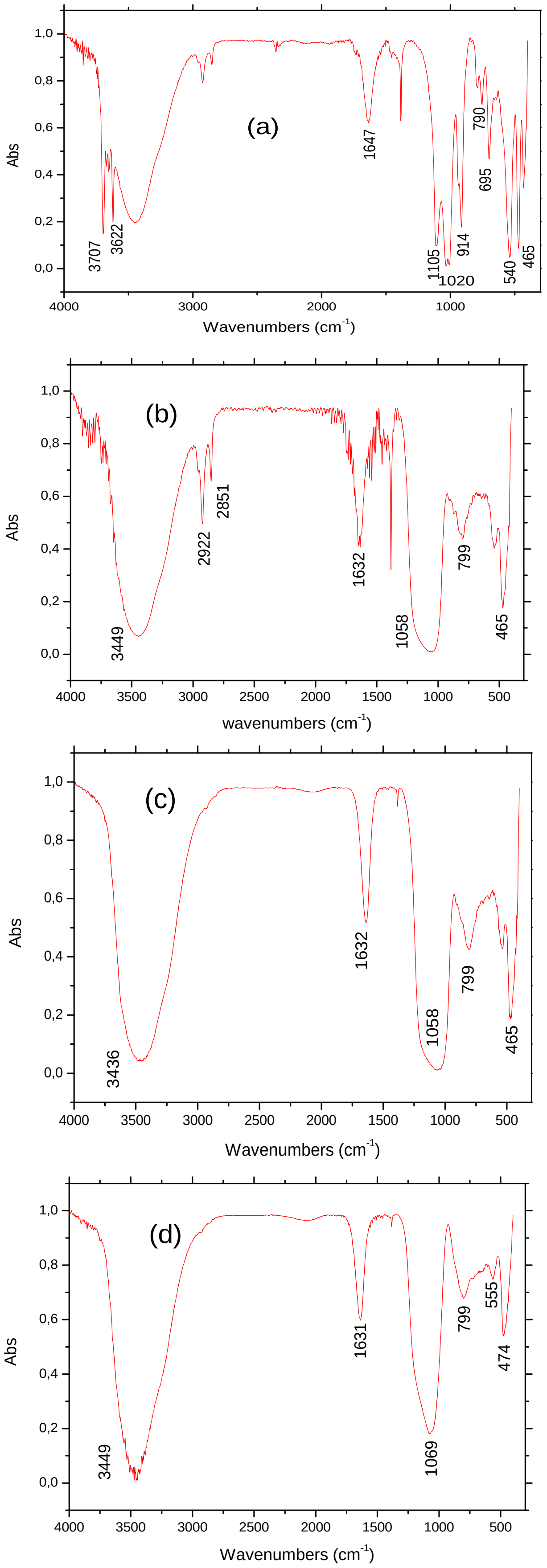

Figure 2 Starting kaolin (a) and thermally treated at 500°C (b), at 550 °C (c), at 700°C (d)

Table 2 shows the different values of metakaolin dissolution enthalpies. The Figure 1 shows the value of the enthalpy according to the dehydroxylation temperature of kaolinite. The estimate on each point can be estimated as being of the order of ± 10 kJ mol^{-1}.

It is found that for a désyhdroxylation between 600 and 700 ° C, one obtains a maximum exotherm for the dissolution of metakaolin in hydrofluoric acid. For temperatures below 700 ° C, the change of dissolution enthalpy is result from the superposition of two endothermic effects: dehydration of kaolin and the changement the state of amorphization of the metakaolin.

From 800 ° C, the onset of recrystallization of metakaolin leads to both a reduction in the reactivity of the solid (decrease in mechanical strength of the binder activated by calcium hydroxide) and a less exothermic dissolution. It is interesting to note that the extrapolation of the curve showing the variation of the enthalpy of dissolution until the value corresponding to the dissolution of kaolinite gives a temperature of 440 ° C for the start of the dehydroxylation of the kaolinite. This result is in agreement with those measured in the literature. The difference between the enthalpy of dissolution of kaolinite and metakaolin heated to 920 °C is of the same order of magnitude as that obtained by Mathurin and al. (Mathurin *et al,* 1986).

IR Results

IR Besides XRD measurements, IR spectroscopy was applied to confirm kaolinite transformation during calcinations. IR spectra obtained for starting clay and ther-mally treated samples are presented in Figure 2. The results of IR spectroscopy of starting clay (Figure 4a) show the characteristic bands of kaolinite (Russel *et al,* 1987): OH− at 3695, 3668, 3651 and 3620 cm^{-1}; Al–OH at 914 cm^{-1}; Si–O at 1020, 1105, 465 cm^{-1} and Si–O–Al^{VI} at 540 cm^{-1}. Absence of the detectable Al–O–H bands at 914 cm^{-1}, and the doublet at 3707 and 3622 cm^{-1}, is evident from Figure 4b–4c-4d. Absence of the band at 540 and 914 cm^{-1} and the appearance of a new band at 799 cm^{-1} can be related to the change from octahedral coordination of Al^{3+} in kaolinite to tetrahedral coordination in metakaolinite. The figure 3 shows the IR of starting kaolinite over the hydroxyl stretching region 3720 to 3580 cm^{-1}.

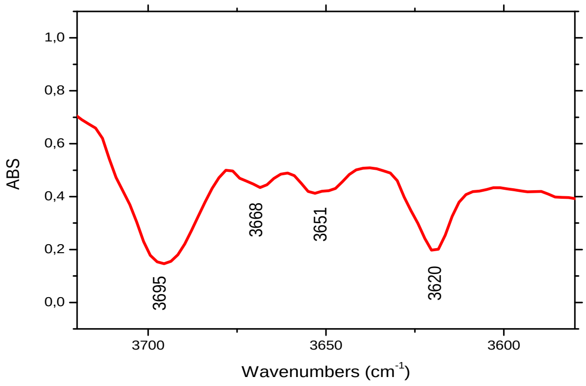

Figure 3 The IR of starting kaolinite over the hydroxyl stretching region 3720 to 3580 cm^{-1}

CONCLUSION

Infrared spectroscopy has been shown to be a very useful spectroscopy technique in the study of the dehydroxylation of the kaolinite clay minerals. Dehydroxylation is complete for a heat treatment of 500 ° C. indeed; we observed the disappearance of the bands for the OH elongation (Figure 2 b). By calorimetry, it is found that for a désyhdroxylation between 600 and 700 °C, one obtains a maximum exotherm for the dissolution of metakaolin in hydrofluoric acid.

Such relatively rapid investigation leading to a fairly accurate characterization of the reactivity (hence the disorganized state of the crystal lattice) of metakaolin based on conditions of dehydroxylation of kaolin could be generalized to two other points concerning clay minerals, namely:

1. Analysis of the formation of high-temperature phases resulting from transitional thermal recrystallization of compounds disordered structure.
2. Quantitative determination test of the state amorphization transitional compounds (metakaolin type) depending on the crystal-chemical characteristics of the starting minerals.

For a désyhdroxylation between 600 and 700 ° C, one obtains a maximum exotherm for the dissolution of metakaolin in hydrofluoric acid.

References

A. Mitrović, Lj. Miličić, B. Ilić (2010). Benefits of use metakaolin in cement-based systems, Treći internacionalni naučno- stručni skup Građevinarstvo – nauka i praksa, Zbornik radova, Žabljak, 15–19, 753–757.

A. Mitrović, R. Đuričić, B. Ilić, B. Živanović (2005). Metakaolin: Nova generacija dopunskih cementnih materijala, Materijali i konstrukcije 48, 48–54.

B. R. Ilic, A. A. Mitrovic, Lj. R. Milicic (2010). Hem. ind. 64 (4) 351–356.

D. Mathurin, M. El M. Chbihi, M. Murat (1986). Thermochimica Acta, 98, 49-55.

D. Mathurin, M. El M. Chbihi, M. Murat (1987). Thermochimica Acta, 122, 79-85.

G. K. Johnson, P. N. Smith and W. N. Hubbard (1973). J. Chem, Thermodyn, 5, 793-809.

J. Bousquet, B. Bonetot, P. Claudy, D. Mathurin and G. Turck (1976). Thermochim Acta, 14, 357-369.

J. Lemaitre, A. J. Leonard and B. Delmon (1982). Bull. Minéral, 105, 501-513.

J.D. Russel, Infrared Spectroscopy Of Inorganic Compounds, Laboratory Methods in Infrared Spectroscopy, Wiley, New York, (1987).

Lawrence C Edomwonyi-Otu, Benjamin Olufemi Aderemi, Abdulkarim Salawudeen Ahmed, Neil J Coville, Malik Maaza (2013). Opticon 1826 15: 5, 1-5. M. Murat, A. Amokrane, J. P. Bastide and L. Montanaro (1992). Clay Minerals 27, 119-130.

M. Murat, M. Driouche (1988). Chemical reactivity of thermally activated clay minerals, Cem. Concr. Res. 18, 221–228.

M. Murat, Y. Arnaud, M. El Moussaouiti and C. Comel (1984). Silicates Industriels, 49, 127-138.

R. Siddique, J. Klaus (2009). Influence of metakaolin on the properties of mortar and concrete: a review, Appl. Clay Sci. 43, 392–400.

Ray L. Frost, and Anthony M. Vassallo (1996). Clays and Clay Minerals, 44, N°5, 635-651.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., and Nuttall, R.L., The NBS Tables of Chemical of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, Vol. 11, Suppl. 2, (1982).

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