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.

Key words: Enthalpie, Kaolinite, Dehydroxylation, Calorimetry, Infrared

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 classified as a new generation of supplementary cementitious 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 or calcination of kaolin clays within a definite temperature range. Metakaolin, pozzolanic additive, may be obtained by 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 a 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 vermiculite (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 Nadorkaolinite (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>
<thead>
<tr>
<th>Table 1 Dissolution tests</th>
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<tr>
<td>concentration of the hydrofluoric acid solution (mol.L⁻¹)</td>
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<tr>
<td>500°C: End of slow dissolution but exploitable experimental curve</td>
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<tr>
<td>720°C: rapid dissolution</td>
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<tr>
<td>980°C: End of slow dissolution</td>
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The dissociation reaction of metakaolin can be schematically presented in the form:

\[ \text{Al}_2\text{O}_3, 2 \text{SiO}_2, \text{m H}_2\text{O(s)} + 24 \text{HF(aq)} \rightarrow 2 \text{H}_2\text{SiF}_6(\text{aq}) + 2 \text{H}_2\text{AlF}_6(\text{aq}) + (7 + \text{m}) \text{H}_2\text{O(aq)} \text{av} \text{c} \leq \text{m} \leq 2 (\text{m} = 2 \text{ for the starting kaolinite}). \]

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

1. HF consumption necessary for the formation of \( \text{H}_2\text{SiF}_6 \) and \( \text{H}_2\text{AlF}_6 \)
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.

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 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 Al₂O₃). 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: 

\[ \text{Al}_2\text{O}_3, 2 \text{SiO}_2, m \text{H}_2\text{O} + 0.0878 \text{SiO}_2 (q) \]

**Thermal effect the HF dilution \( \Delta H_1 \)**

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 Al₂O₃, 2 SiO₂, m H₂O dissolved in a solution of hydrofluoric acid (HF, x H₂O), 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:

\[ h = \frac{d[\Delta H^0_1(HF, xH_2O)]}{dx} \]

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

\[ \Delta H_1 = -400(91 + m) \text{ J.mol}^{-1} \]

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 \( \Delta H_2 \)**

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

\[ \text{SiO}_2(q) + 6 \text{HF (aq)} \rightarrow \text{H}_2\text{SiF}_6(\text{aq}) + 2 \text{H}_2\text{O (aq)} \]

The heat of this reaction is of the order of -140 kJ mol\(^{-1}\) (Wagman et al., 1982), therefore a thermal effect \( \Delta H_2 \) 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 déshydroxylation 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–Al⁴⁺ 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 Al³⁺ 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.

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

References


How to cite this article:
Sandhya rani T et al., Incidence Of Malaria And Typhoid In Acute Fever In Tertiary Care Hospital Around Pondicherry. *International Journal of Recent Scientific Research* Vol. 6, Issue, 6, pp.4444-4448, June, 2015

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