A Comparative study by conductivity measurement of polarisation of hydratation mechanism of bentonites

A.Sassi[1]*, Z.Derriche, A.Djebaili[2], J.C.Giuntini[3]

[1]Laboratoire de Science des Materiaux Universite des Sciences et de la Technologie Oran, (ALGERIE)

[2]Laboratoire D'etude des Materiaux Organiques - Universite de Batna - (ALGERIE)

[3]Laboratoire de Physicochimie de la Matiere Condensee Faculte des Sciences Montpellier, (FRANCE)

Telephone : +213-76465648; Fax : +213-33-868975

E-mail : ahmed_sassi@yahoo.fr

ABSTRACT

The conductivity of polarisation was measured at equilibrium with a water vapour pressure ranging from 1kHz to 1MHz; the temperature was maintained constant at 298°K all along this study. The measurements were then monitored by the relative water vapour pressure (P/Po). We notice that water adsorption creates in the sample a significant increase in dipole number. This study allows showing transport proprieties in these disorder solids. During bentonite hydratation and under the influence of compensator cations (Na+ and Ca++), the swelling phenomenon affects considerably the conductivity. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

The bentonites are well known materials since very long times, the basic structure is tridimensionnal made of superpositioned layers. The unit cell is monoclinic with two patterns whose crystalline parameters are as the following:

$a = 5,2\lambda$Å ; 8,8 A$\leq\beta\leq$ 9,2 Å ; 95°C$\leq\beta\leq$ 100°C

The parameter (C) is not constant and depends of the nature of compensator cation and the quantity of water adsorbed, the distance between the sheets is hence variable in the direction[001], at dry state for the bentonites, it is in the range 9,4 et 10? . Each crystal consists of tens of sheets that determine the adsorption properties, which are often similar to those of colloids.

The bentonites are swelling clays characterised by one sheet that consists of an octaedric layer incorporated between two tetraedric layers (figure 1a) and a number of water layers. We have carried out in this work a comparative study by the conductivity measurements
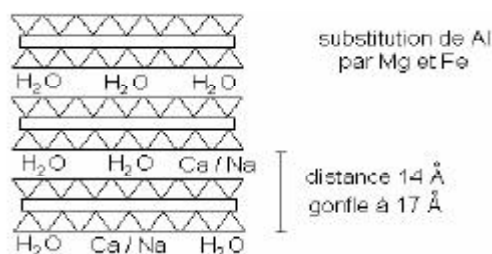

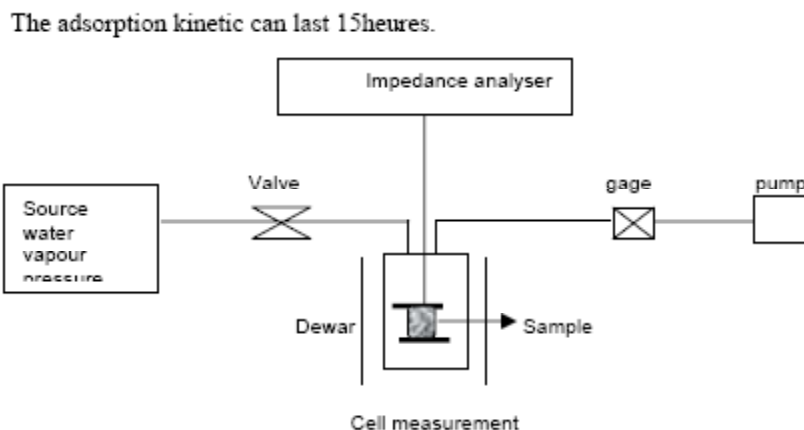**Figure 1a : Show the octaedric and tetraedric sequences in a bentonite**

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The adsorption kinetic can last 15heures.

Figure 1b: The conductivity measurement set up as a function of the water vapour pressure

TABLE 1: Chemical composition (w %) of the original clay

SiO₂	Al₂O₃	Fe₂O₃	MgO	TiO₂	Na₂O	K₂O	CaO	SiO₂ / Al₂O₃
65,36	13	2,29	2,11	0,19	1,55	1,55	4,48	5,02

TABLE 2 : Chemical composition (%) after exchange

Elements	Si	Al	Na	Ti	Ca	Fe	Mg	K
Bentonite- Na	21,30	9,50	1,65	0,08	0,70	2,35	1,30	0,40
Bentonite- Ca	20,35	8,50	0,10	0,05	3,05	2,40	1,60	1,35

of a bentonite polarisation exchanged in sodium then calcium.

We hoped to extend this study to see the fundamental mechanisms which are involved during water vapour adsorption. To this end, models of interpretative type were implemented to take into account these phenomena.

EXPERIMENTAL

The material used is a bentonite of the Algerian North West, the chemical analyses is given in TABLE 1. The material undergoes a number of treatments in order to eliminate impurities[1]; the product obtained that is the clay fraction of size less than 2μm is saturated by a solution 1M of NaCl (test AgNO3), one part of the prepared clay is transformed into calcareous clay in the same way. The results are shown in TABLE 2. The samples are in the form of thin films (thickness of the order of 0,3mm) dried then placed between two copper electrodes inside the measurement cell.

The set is similar to an RC circuit in parallel. An alternating signal of a given frequency is applied is followed by a response supplied by an impedance analyser that allows to monitor the values of the conductance and the capacitance. The experimental set up is illustrated in figure 1b.

The water cylinder is isolated from the cell by means of a metallic valve until full degassing is achieved. The cylinder is placed in liquid nitrogen. The hole system(cylinder and cell) is degassed and pumped until a vacuum better than 10-3 torr is obtained(valve opened). When this pressure is reached the cell is again isolated from the cylinder and will be placed in a cryostatic bath which maintains the temperature between(-25 and +16⁰C±5⁰C), hence the temperature determines the water vapour pressure to which the samples will be submitted. When the cylinder and the cell are made in contact we can then have access to the electric property as a function of P/Po ratio.

P : saturation vapour pressure at the sample temperature; Po : water vapour pressure at equilibrium with the sample

EXPERIMENTAL RESULTS

The figure 2 and 3 illustrate the variations of the conductivity as a function of relative water vapour pressure (P /P0) at 298⁰K between 1KHz et 1MHz for sodic and calcareous bentonites; the measurements
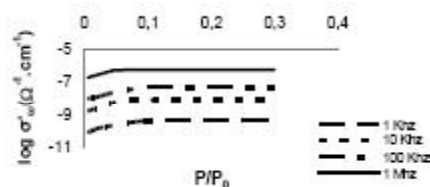

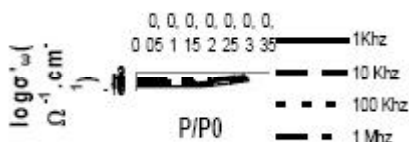**Figure 2: Variation de la conductivite de polarisation en fonctiondela pression relative de la vapeur d'eau a differentes frequencespour une bentonite sodium**

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Figure 3: Variation de la conductivite de polarisation en fonction dela Pression relative de la vapeur d'eau a

show that a conductivity of polarisation '(ω) appears when the samples are submitted to an alternating electric field.

It is more often linked to the field impulse imposed by the relation:

$$\sigma'(\omega) = A(T)\omega^s$$

The conductivity increases linearly in a logarithmic scale, where S is the gradient. The conductivity is due to a transport of charges by hopping between localised sites[2,3]. References[4,5] suggest that current transport in clays is attributed to protons movements between the defects, we made the simplified assumption of protons movement at the clay surface as a diffusion movement [6-8].

We can estimate the polarisation conductivity due to adsorbed water[9-13].

$$\sigma'(\omega) = 8\pi N^2 \frac{e}{3}\left(\frac{e^2}{\varepsilon W_M}\right)\left(\frac{1}{\tau_o}\right)^\beta \omega \int_{\tau 0}^{\tau oo} \frac{\tau^\beta \omega d\tau}{\omega\tau^2}$$

N: number of sites; WM: activation energy ; (ω) : angular frequency; τ: relaxation time; τo : the inverse of proton vibration frequency trapped in the site; ε : dielectric constant; β = 2kt/WM

DISCUSSION

For sodic bentonite (figure 2), in the frequency range studied, we notice that for relative water vapour pressures (P/Po<0,1) the conductivity varies in a linear manner with the P/Po ratio. In this case, the sheets are still not opened.

The water is found localised between interreticular spaces, we see adsorption of particles on the boundary and lateral surfaces. This state is called "macro swelling".

When (0,1<P/Po<0,3) a step-like behaviour appears, which indicates the opening of sheets, the water is found trapped between inter-foil and does not con-tribute to the conduction phenomenon, the filling continues until a first water layer is obtained. This state is called "micro swelling".

In the case of calcareous bentonite (figure 3), the sheets opening occurs in the range (P/Po< 0,1) where water is found localised between the sheets and does not participate to the conduction phenomena that leads to existence of a step. When (0,1<P/Po<0,3), the conductivity increases with P/Po ratio in the same frequency range. In this case water does not affect inter-foil spaces and is localised on the boundary and lateral sheet surfaces.

CONCLUSION

During exchanges by monovalent cations (Na+), hydratation water is fixed on oxygen atoms forming the boundary layers of sheets in a continuous manner. We notice often, in the case of sodic bentonite a shift of sheets of the order of 12,5Å

Corresponding to water layer. The monovalent cations are not incorporated in hydratation layers but remain fixed in hexagonal cavities of the sheets.

The calcareous bentonite gives directly two water layers, hydratation continues until the spacing of the sheets reaches 15,4Å. Corresponding to two water layers, in this case, hydratation water is fixed around the cation, inter-foil water is arranged in molecular plane layers with a succession of hydrates at one, two and three successive equidistant molecular layers(12,5 15,5 18,5Å) with spacing equals to 3Å, which is equivalent to a water layer thickness.

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