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Contribution to Characterization of Natural Diatomite

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***Abstract*— With the complex examination of raw material from a Sig deposit in Algeria in the region of Mascara area, physical, chemical and mineralogical properties of diatomite have been defined. It has been found that it is a dominantly amorphous material, sedimentary rock of the type silica-diatomite. The raw material consists of approximately 60% SiO_2. Among the physical properties, we find a porosity of 60%, which constitutes a wide range of practical application, in various fields, absorbing, insulating, natural insecticide, and filter water etc. For determination of the chemical contents, properties and origin of the raw material, the following methods have been used, such as, chemical analysis, X-Ray diffraction analysis, optical microscopy (SEM). The Thermo-Gravimetric (DSC/TGA) analysis was obtained simultaneously using a TA Instruments Universal Analysis 4.5A. The samples were heated at a rate of 10°C/min, from room temperature to 1200 °C in a static air environment. The results show the different peaks of transformation as well as mass losses at different temperatures.**

***Keywords*— Diatomite, DSC, X-Ray, Kieselguhr, Sig**

I. INTRODUCTION

Natural diatomite was obtained from the Sig area of Mascara in Algeria. Diatomite is a well-known natural product, it carries several name, namely: kieselguhr, diatomaceous earth, diatomite, diatomaceous earth, tripoli, and diatomaceous flour. This is a clear colored rock consisting primarily of silica and impurities (organic compounds, sand, clay, calcium carbonate and magnesium, salts) [1]. Diatomite used for the manufacture of cements, clay diet, bricks [2], adsorbents, filter powders, fillers, and catalysts [3], [4]. As a siliceous rock made up largely from diatoms, diatomite has a unique combination of physical and chemical properties, making it applicable for the removal of heavy metals and organic pollutants, and as a filtration medium in a number of industrial uses [5], [6]. For its high permeability, high porosity and chemical inertness, many studies [7]-[9] have been tested as an absorbent product, used to remove dyes. These applications include also filter aid, functional filler, insulation, catalysis support, and carrier application [10]-[12]. Most research is focused on the adsorption properties of diatomite. The application of diatomite in the field of wastewater treatment is highly dependent on its origin and further efforts are needed to improve its adsorption capacity [13]. Porous ceramics supports are, generally needed for membranes. For the development of hight quality supports, it's very important to have pore size distribution, total porosity ratio, surface quality, good mechanical properties and chemical stability. The use of ceramic membranes has many advantages such as higher thermal and chemical stability, pressure resistance, long lifetime and catalytic properties from their intrinsic nature [14]. Silica is a raw material that finds its importance and its application in several sectors. It is a raw material in the ceramic industry and most refractory bricks. Silica is found in nature in crystalline form (quartz, cristobalite and tridymite), cryptocrystalline (chalcedony) and amorphous (opal); its density and its melting point vary according to the crystalline form [15].

Diatomite has high porosity (> 50%) and low permeability [16]. Application of diatomite on the wastewater treatment depends mightily on its origin and a more efforts should be attempted to enhance its adsorption capability [17]. For more than 50 years, diatomite of lower purity has been used to absorb liquid spills [18]. Both granules and powders of various grades are manufactured and may be calcined to increase hardness, improve durability after absorbing a fluid and reduce the tendency to produce dust [19]. Some researchers have determined the potential efficacy of insecticides against stored-product pests. Their work is based on the preparation of diatomite samples with different size fractions: 0-20 (µm), 0-45 µm, 0-150 µm, 20-45 µm and 45-150 µm. They found that the diatomite sample with 45 µm grains was the most efficient [20]. Other researchers have used diatomite as an insecticide for corn weevil. From the fact that inert dusts such as diatomaceous earth are physical insecticides that would alter the water balance and cause the death of insects by desiccation. They were able to develop a formula that affects the water balance: a fundamental component of insect homeostasis. They evaluated the activity of two diatomite formulations on a harmful species of cereals stored in hot climates. They tracked their actions on insect tegument and water balance alterations in a relative humidity range, assessing their effect on insect water content and water

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loss rate. Both formulations compromise insect survival across the range of relative humidity tested (ie from 0 to 100%), reducing the median survival time by one-third. Both formulations damaged the surface of the insect tegument, including sensilla and pores, and compromised the water balance by reducing the body's water content and increasing the rate of water loss more that double [21]. In another research work, five series of bioassays were performed using Petri dishes with their separate bottoms in two equal parts. When the diatomite tested were applied in combination with spinosad, its presence negatively affected contact preference, particularly in the case of larvae. The results of this work indicate specific behavioral responses of insect products stored insecticide formulations, which can strongly affect the effectiveness of control strategies [22].

Membrane bioreactor (MBR) has attracted great attention in municipal and industrial wastewater treatment and reclamation in recent years [23]–[26]. Additionally, the dynamic membrane formed on the big pore mesh could increase the intrinsic membrane retention capacity [27]–[30].

The Sig diatomite deposit as presented on Figure 1, is located 5 km south-east of the town of Sig, 50 km from the city of Oran and 40 km from the town of Mascara.

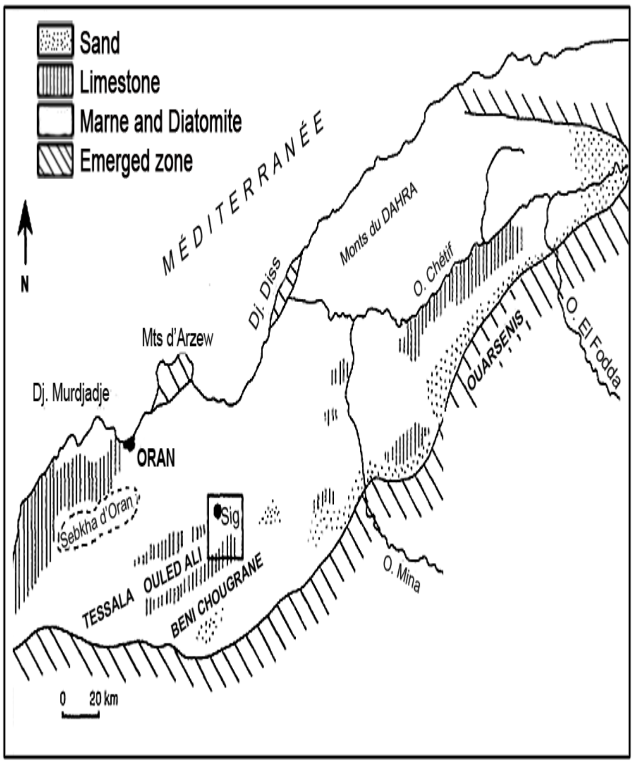

Fig. 1 Geographical localization of the layer of diatomite

II. EXPERIMENTAL PROCEDURE

Chemical and phase analyses of the diatomite sample were conducted using X-ray fluorescence (XRF). In X-ray fluorescence (XRF) spectrometry, the characteristic spectral line radiation emitted by the analyte is measured to determine the concentration. Theoretical relationship is based on X-ray physics and measured values of fundamental atomic parameters in the X-ray region of the electromagnetic spectrum [31]. X-ray diffraction is one of the most successful tools which are used precisely for identification of crystalline phases. The phase's compositions of the materials were characterized by X-ray powder diffraction technique [32], [33].

The acquisition of X-ray diffraction was carried out on a ULTIMA IV Rugaku powder diffractometer with a Cu anode as a source of RX (characteristic wavelength. The device has been used in configuration Bragg-Brentano.The morphology and microstructure of the materials were studied by using PHILIPS XL 30 scanning electron microscopy (SEM) technique. Scanning Electron Microscopy is an electronic microscopy technique capable of producing high resolution images of the surface of a sample using the principle of electron-matter interactions.

In thermal analysis, several characterization techniques are used. The choice of the technique depends on the desired results. Table 1 illustrates the different thermal characterization techniques according to the expected results [34].

	DTA (T)	DSC (T, H)	TGA (Δm)
Glass Transition	+	+ +	
Fusion	+ +	+ +	
Purity		+ +	
Evaporation	+	+ +	+
Sublimation	+	+	+
Phase Change	+ +	+ +	
Cristallization	+	+ +	
Pyrolysis	+	+	+ +
Curie point	+	+	

TABLE 1: Different thermal characterization techniques

With:
T for the temperature measurement
H for enthalpy,
Δm for the variation of the mass,
+ means the importance of this measurement technique of which ++ means that this technique is best suited to measure this property,
DTA is the Differential thermal analysis
DSC is Differential scanning calorimetry
TGA is Thermogravimetric analysis

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Simultaneous thermal analyser, differential scanning calorimetry and thermogravimetry analysis (DSC-TGA) were carried out using a fully computerized TA Instruments Universal Analysis 4.5A. This analysis is used to investigate physical and chemical processes related to thermal effects such as phase transitions and mass changes due to evaporation and decomposition of the sample. The tests were carried out under the same experimental conditions, about 10 mg of product were placed in an alumina crucible for simultaneous thermal analysis (TGA-DSC) and heated at a rate of 10°C/min, from room temperature to 1200 °C in a static air environment.

Particle size analysis The tests were carried out in an air vacuum sieve in accordance with standard NF X 11-640. The vacuum air sieve has a circular screen in a sealed housing inside which open two pipes, one air inlet, the other suction. The housing is equipped with a transparent cover, which makes it possible to monitor the sieving operation. The air supply line terminates in a rotating nozzle provided with a longitudinal slot disposed radially under the screen and at a very short distance from it. The nozzle is mechanically driven in a rotational manner so as to continually sweep the lower surface of the screen with an air jet for holding the particles in suspension. The test procedure is as follows: - Securing the sieve on the sifter - Weighing the product to be sieved and put it on the sieve mounted on the sieving apparatus - Put the transparent lid on the sieve - Adjusting the amount of air drawn in order to obtain an optimal vacuum - Switching on the sieving device and the suction system for a fixed period. - After having stopped the device, weigh the mass remaining on the sieve - Install the following sieve, and so on until the end.

III. MAIN RESULTS

Chemical composition of diatomite sample were conducted using X-ray fluorescence (XRF) and presented in Table 2, shows the predominance of silica and lime with alumina and iron oxide in lower proportion. The minerals represented by K_2O, SO_3 and Fe_2O_3 contents were found as impurities in the. SiO_2 which is the body builder of raw diatomite was found to be amorphous as opal-A mineral.

Elements	Concentration (%)
Al_2O_3	2,65
SiO_2	60,28
P_2O_5	0,07
SO_3	0,12
K_2O	0,67
CaO	5,50
Fe_2O_3	0,91

TABLE 2: Chemical analysis of original diatomite sample.

The X-ray spectrum of the raw diatomite sample presented in Figure 2, shown the existence of calcite, Quartz and Ankerite.

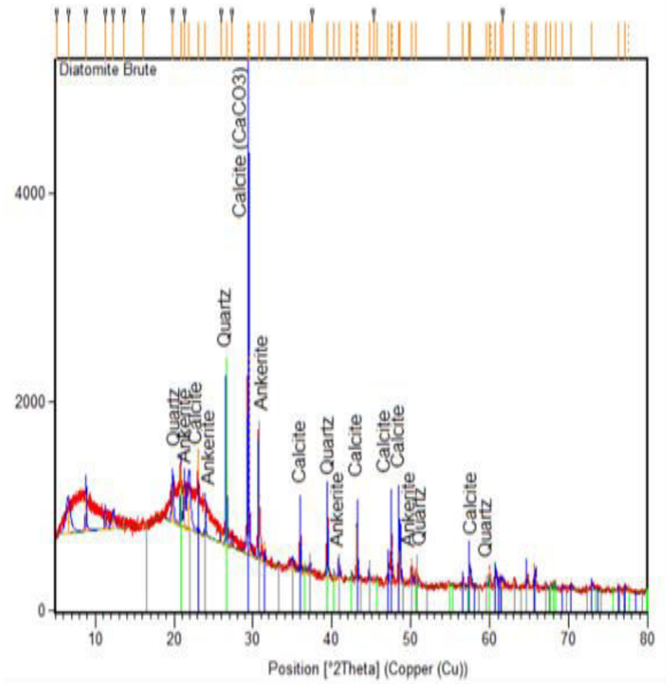

Fig. 2 XRD Patterns of Diatomite original Sample

The mineralogical composition of the examined sample from Sig region which was identified and is shown in Figure 2.

The composition consists mainly of calcite, quartz and ankerite. The results of diatomite by scanning electron microscopy (SEM) with a magnification of 500 X (Figure 3) and 1000X (Figure 4), shown that diatomite has a porous structure in the form of a honeycomb with impurities that can eliminate by calcination.

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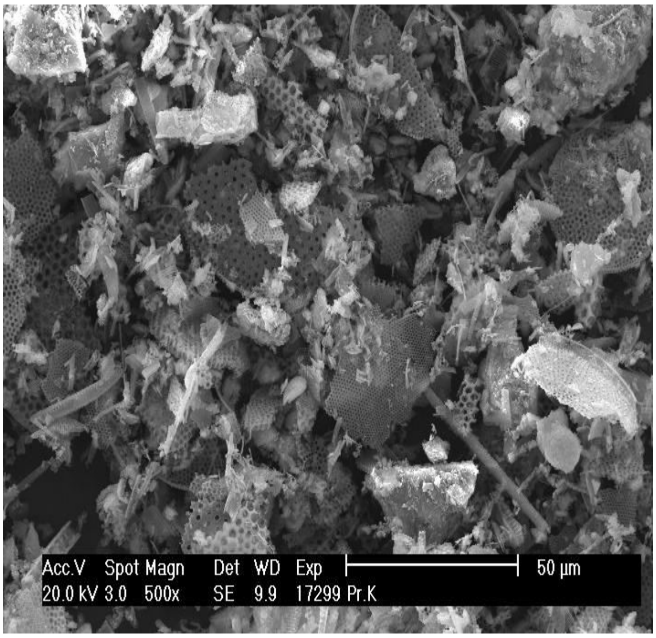

Fig. 3 SEM micrography of the diatomite powder

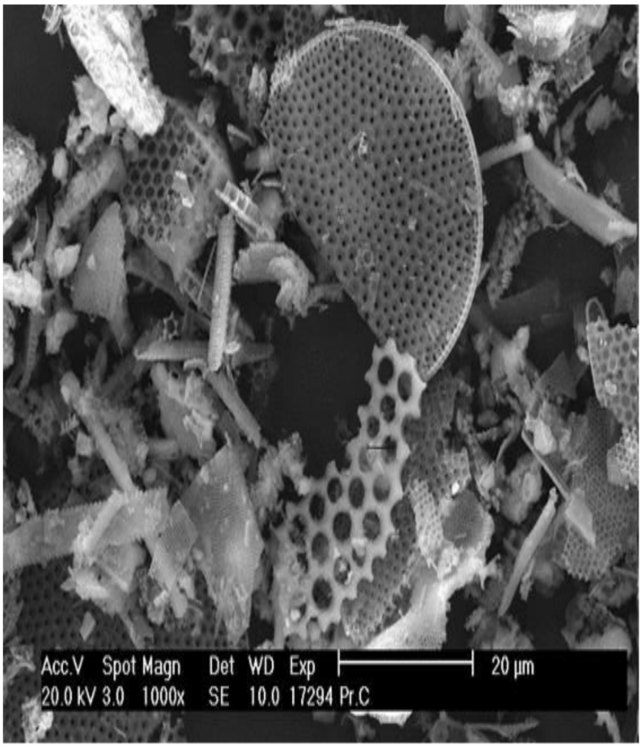

Fig. 4 SEM micrography of the diatomite powder

The results of experiments thermal analysis were performed in a TA Instruments Universal Analysis 4.5A, are shown in Figure 5.
The results obtained on three samples of diatomite powder mass 10 and 10.003 mg are reported in Table 3.

	10 mg			10,003 mg		
Diameter	Detention	Past	%	Detention	Past	%
< 32	5,85	4,14	49,11	7,31	2,68	31,66
45	4,48	1,37	16,28	4,76	2,55	30,12
63	3,53	0,94	11,17	3,91	0,84	10,00
90	2,74	0,79	9,42	2,72	1,19	14,05
125	2,13	0,60	7,16	2,09	0,62	7,42
> 200	1,56	0,57	6,83	1,52	0,57	6,73

TABLE 3: Result of granulometric analysis

From the results of the sieving obtained, we find that more than 80% of the mass of the product is formed from grains of 90 to 200 microns.

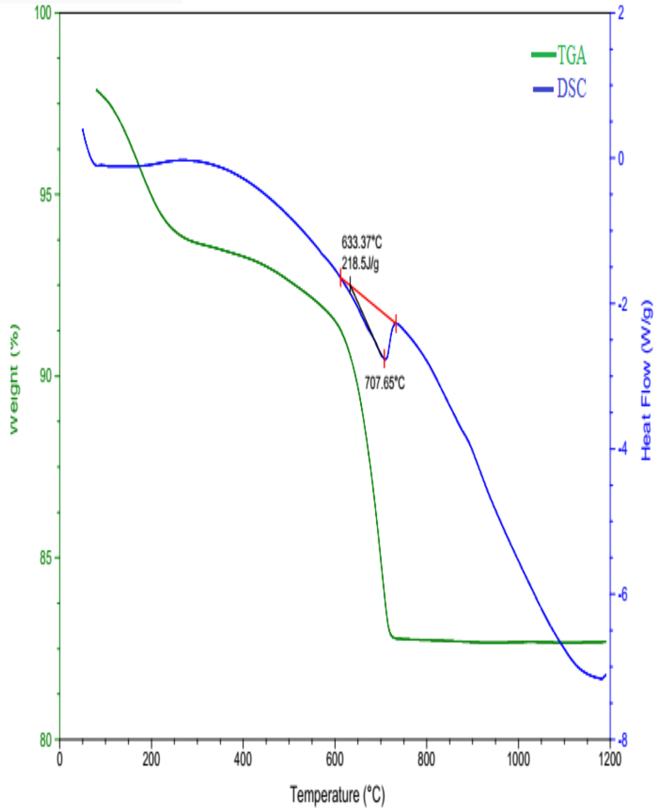

Fig. 5 Simultaneous thermal analysis TGA-DSC for diatomite sample

We see a total weight loss of 17% at 1200 ° C occurring in several steps. The first weight loss is associated with endothermic peak due to evaporation of absorbed moisture. The second weight loss is about 06 % observed at 260 °C and the last mass loss between 633.37°C and 707.65 °C is divided in two steps. The first mass loss (8 %) is due to burning of residual part and dehydroxylation and the last weight loss (09 %). Thermal reactions associated with weight loss shows two endothermic.
The first endothermic peak is at 84.7 °C and the second peak at 707.65 °C corresponds to α ↔ β quartz transformation.

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IV. CONCLUSIONS

The results of characterization of diatomite from a Sig deposit in Algeria show the predominance of silica, alumina, lime and iron, whereas all the other major and the trace elements are in low concentrations However, the main quartz and calcite lines are distinguished. During the observation on SEM, it appears clearly a porous microstructure in the shape of honeycomb. Coupled thermogravimetric and differential calorimetry (DSC / TGA) thermal analysis, gave us a good approach to the thermal and mass evolution of the sample according to the temperature. The results show a significant loss of mass for diatomite of the order of 17 %, and the four peak transformation at different temperature. From the results of the investigation carried out, it can be concluded that the natural diatomite from the Sig deposit may find application for obtaining of ceramic membranes for water filtration. the results of sieve size measurements show that more than 80% of the mass of the product is formed from grains of 90 to 200 microns

The results of the thermal study of the samples examined after heating up to 1 200°C, at a rate of 10° min^{-1} shown in Figure 5:

- In the temperature range from 25°C to 100°C, the weight loss due to absorbed water is about 3%.
- The crystalline water contained in the opal-A is lost at about 120 degrees [24]
- In the temperature range from 400°C to 500°C, the weight loss (3.5) is characteristic peak on the TGA curve, which extends up to the temperature of about 600°C. This is attributed to the dehydroxylation of the ankerite.
- The about 633°C and 750°C peaks on the TGA curve correspond to endothermic pic.

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