Microscopic evaluation of diatomite for advanced applications: Case study

A.Q.Selim¹, A.A.El-Midany², and S.S.Ibrahim³

¹Geology Dept., Faculty of Science, Beni Suef University, Egypt
²Mining, Petroleum, and Metallurgy Dept. Faculty of Engineering, Cairo University, Egypt
³Central Metallurgical R&D Institute, P.O. Box 87, Helwan, Egypt.

Diatomaceous materials from Kom-Osheam, Egypt were microscopically investigated to determine their characteristics, ways of processing (purification) and their specifications for industrial applications. Such microscopic study used different techniques of microscopy such as; optical microscopy, scanning electron microscope (SEM) and transmission electron microscope (TEM).

Optical microscope revealed that the diatomite is composed of diatomaceous skeletons (frustules), clay minerals, calcite, quartz and heavy minerals. Diatomite contains different genera and species which are related to pinnate, centric, platy and acicular forms. Finally textural features, geometrical shapes and pore shapes and sizes are anatomized by using the optical microscope.

The raw sample is subjected to soaking followed by attrition scrubbing to reject most of the silt contaminations above 74 microns. Hydro-cyclone classification was applied to separate the rest of the silt minerals (-74 + 45 microns) as well as to produce a diatomite pre-concentrate of -45 micron and another diatomite–rich clayey fraction below 10-5 microns. The pre-concentrate fraction was treated by thermal, acid and thermal-acid methods.

Scanning electron micrographs showed the presence of different skeleton forms and their morphological characteristics. It is clearly that there are many of complete intact diatomite skeletons that have complex structure with numerous fine microscopic pores, cavities and channels.

TEM observations of diatomite exhibit smooth clean surface with well-opened pores and connected channels. Microstructure analysis shows micro-pores of variable shapes, sizes and pore spaces. Most of the pores are well-opened and all impurities are outside diatomite pores, which have a significant influence on technological process design. Certain diatomite frustules display a high density of regularly ordered pores with diameter from 100 to 600 nm. The pores are arranged in parallel sets with uniform pore spaces giving a honey-combs structure.

Structural changes of the sintered diatomite are thoroughly examined through the microscopes to select the effective treatment conditions. The physical properties of produced diatomite meet the specifications of various industrial applications, such as catalyst supports, filtering aids and production of meso-pores materials.

Keywords microscopic investigation, optical microscope, scanning electron microscope, transmission electron microscope

1. Introduction

Diatomite is a silica mineral composed of the fossilized skeletal remains of microscopic single-celled aquatic plants (algae) called diatoms. Over 10,000 species of microscopic algae’s have been recognized, each one has its own distinct shape and ranging in size from below 5 microns to above 100 microns. Diatomite deposits are of sedimentary origin that is consisting mainly of the accumulation of the skeletons which were formed as the external protective coverage for the aquatic floating algae or diatoms. These skeletons are amorphous hydrated or opaline silica. Normally, the diatomite deposits not only consists of diatom shells, but also contains other sediments like clay, inorganic carbonates, iron oxides, and fine sand, [1-2].

Diatomite has many important industrial applications due to its unique properties, i.e. micronized and sub-micronized porous structure, light-weight, and chemical inertness. These applications include filter aid, functional filler, insulation, catalysis support, and carrier application, [3-12].

Egypt is blessed with huge reserves of diatomite deposits, especially in El-Fayoum Depression. Diatomite deposits in Egypt were studied by several authors [13-21]. The physico-chemical properties of these diatomites can not be used directly unless they are modified. The aim of the present microscopic study was to evaluate, purify and determine Kom-Osheam diatomites characteristics needed for advanced applications.

2. Materials and methods

Different representative samples from well-exposed outcrops or shallow trenches as well as samples representing all the different facies forming the deposit sediments were collected. The sample was gently and thoroughly crushed to -10 mm then transferred to the "Denver" attrition scrubber at 40% solids, in closed circuit with 74µm "Russell" vibrating
screen. The over screen product i.e. +74 µm was collected and dried for storage. The under screen (i.e. -74 µm) pulp was subjected to separation by 3-inch “Mozley” hydrocyclone. The hydrocyclone products (overflow and underflow) were collected, dried and directed to evaluation. The over flow product, supposed diatomite-rich product, was directed to thermal and acid treatments in order to enrich them in silica and enhance some of their technical properties.

The processed diatomite was calcined at different temperatures 600°C, 900°C, 1000°C, and 1100°C, 1200°C for 5 hours. Calcinations were carried out in a programmable furnace, with 20°C/min heating rate. On the other hand, the acid treatments were carried out with commercial sulfuric acid (1:3 solid to acid). Thermal and acid treatments include, heating the processed diatomite to 550°C for 24 hours then leaching either at room temperature for 24 hours or by drying at 100°C for 3 hours.

Chemical and phase analyses of the raw, classified and treated samples were conducted using X-ray fluorescence (XRF) and X-ray diffraction (XRD). The skeletal diatomite in the pre-concentrate as well as in the final beneficiated product was microscopically investigated by optical microscope and PHILLIPS X L30 scanning electron microscope (SEM). Microstructure analysis, using JSM T-20, JEOL transmission electron microscope (TEM), provides reliable information about shape, structure, pore spaces and sizes of diatom frustules.

3. Microscopic evaluation

3.1. Crude sample

Diatomaceous earth deposits are recorded in the northern part of El-Fayoum Governorate, Egypt (Kom-Osheam) in the form of isolated patches or disconnected outcrops of low elevation forming low-lying topography. The diatomaceous earth deposits in this area are generally fine-grained, friable to slightly hard rocks ranging in color from white, grayish white, yellowish white and white with brownish shades. It occurs as different horizons of variable thicknesses intercalated with sand and silt. Mineralogical investigation of Kom-Osheam original sample, using optical microscopy and XRD analysis, showed that the sample is composed of diatomaceous skeletons (frustules), clay minerals (kaolinite and montmorillonite), quartz, carbonates, some heavy minerals, and organic matters (Fig.1). The XRD of the sample depicted clearly the highly crystalline peaks of calcite, clays, quartz, beside the amorphous peak of diatomite phase. The two types of carbonates, calcite and dolomite, were quite detected (Fig.2). Table 1 illustrated the chemical analysis of the sample, which confirming the predicted XRD phase analysis of the ore.

![Fig.1](image1.png) Microscopic photos show the mineral composition of the diatomite original sample, the form and the appearance of the frustules, (a) PPL, (b) CN.
Fig. 2 XRD Patterns of Kom-Osheem Diatomite Original Sample

Table 1. Chemical Analysis of Original Sample

<table>
<thead>
<tr>
<th>Constituent</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>L.O.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>74.20</td>
<td>3.55</td>
<td>10.58</td>
<td>3.37</td>
<td>8.3</td>
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</table>

SEM investigation of the crude sample exhibit diatomite frustules with closed-pores dispersed in clay and carbonate matrix (Fig. 3 a &b).

Fig. 3 SEM micrographs of; (a) crude diatomite sample , (b) close-up view on pores of centric frustules.

3.2. Processed diatomite

After attrition scrubbing, the over screen (+74 µm), containing silica sand and shell remains as main components, was rejected. Microscopic evaluations of the classified diatomite (overflow fraction) revealed the presence of intact diatomite skeletons, however, it is not clearly observed in addition to the skeletons surfaces were partly masked by the impurities; meanwhile the pores were filled with minute minerals and organic grains (Fig. 4 and 5).
Figure 4: Microscopic Photographs (PPL) of the overflow Classified Diatomite Product Showing: [a] Appearance of diatom skeletons, notice the heavy grain impurities. [b] Close-up view on pinnate diatom skeletons.

Figure 5: SEM micrographs of: (a) classified diatomite sample, (b) close-up view on centric diatom form.

Figure 6 shows the microscopic examination of the diatomite after firing at different temperatures. The surfaces of the frustules after firing at 600°C show clean and clear pores (Fig. 6a&b). Calcination at 900°C for 3 hours is favorable condition because it removes or reduces the impurity levels without structural changes (Fig. 6c&d). Thermal treatments above 900°C or at 900°C for longer times give the same results; however, these conditions lead to damage and collapse of the diatom skeletal structures (Fig. 6e and f).

Combined thermal-acid treatment shows the best results. Calcinations at 550°C for 24 hours followed by leaching with concentrated sulphuric acid (1:3 solid to acid) for 24 hours at room temperature or for 3 hours at 100°C are recommended. The morphology of the frustules and the original geometry of the pores are well preserved. The samples calcined and then leached with cold and hot acid have been examined carefully under the optical microscope (Fig. 7). No significant mineralogical variation between classified samples and leached ones with cold or hot acid. However, the latter sample is very white and brighter. The results indicated that the clay minerals and calcite can be removed more easily with acid leaching after thermal treatment. The same findings were observed under SEM (Fig. 8).
Fig. 6 Optical microscopy photographs (PPL) showing frustules of calcined diatomite at: a-600°C for 5h, b- close up view on (a), c-900°C for 3h, d- close up view on (c), e-1000°C for 5h, f- close up view on (e).

Fig. 7 Optical microscopy photographs (PPL) show general appearance and close-up view of different diatom species after thermal-acid treatment.
3.3. Diatomite final product

Morphological and textural Characteristics; pore shapes and sizes of the diatomite final product are shown in figure 9. It is clear that for most part of the sample there are many complete intact diatomites and are less-damaged. They have complex structure with numerous fine microscopic pores, cavities and channels. The length of the channels is about 4 µm and the spacing between adjacent channels (striate) is species specific and typically varies from ~ 10 to 2 µm. Their pores are about 500 nm.

Fig.9 SEM micrographs showing morphology, pore shape and pore size of diatomite final product; (a&b) pores and channels for disk-shaped diatoms, (c-f) detail pore shape and size for pinnate diatoms, (g) acicular and platy diatoms, (h) detail of pore size for platy diatoms.
TEM observations of concentrated diatomite exhibit smooth clean surface with well-opened pores and seriate edge (Fig.10 a &b). Certain diatomite frustules display a high density of regularly ordered pores with diameter from 100 to 600 nm (Fig.10 c). The pores are arranged in parallel sets with uniform pore spaces giving a honey-comb structure, (Fig.10 d). Examination of porous structure reveals varieties of rigid shapes and open voids; occasionally they are locked by rounded particles of the retained impurities (Fig. 10 e).

Fig.10 TEM Photographs of concentrated diatomite show arrangement and details of porous structure; (a) platy and pinnate diatoms; magnification of 4000x, (b) pinnate form with seriate edge, magnification of 10000x, (c) rounded to semi rounded pores; magnification of 20000x (d) arrangement of pores; magnification of 10000x, (e) acicular diatom; magnification of 10000x.
4. Conclusions

Diatomite Earth from Kom-Osheem, El-Fayoum, Egypt was investigated. Microscopic, chemical and XRD evaluation of the representative sample showed that the diatomite of this deposit was moderate in grade, where its silica content was about 50%, and calcite was the main impurity associated with quartz and clays.

Processing of the sample included gentle crushing followed by attrition scrubbing in closed circuit with 74 micron screen. The under screen product was subjected to a 3 "Mozely" Hydro-cyclone to reject the silt remains above 45 micron.

The dried -45 micron product was directed to calcinations at different temperatures between 600°C -1200°C for 5 h. The results showed that calcinations at 900°C for 3 h improved the diatomite pores structure, while calcinations above 1000°C destroyed it. These results were recorded by optical microscopy, XRD and SEM techniques.

It was found that leaching with hot H₂SO₄, without calcinations, is more effective than leaching with cold H₂SO₄. Thermal-acid treatments showed the best results. Calcinations at 550°C for 24 hours followed by leaching with concentrated sulphuric acid (1:3 solid to acid) for 24 hours at room temperature or for 3 hours at 100°C are recommended. The morphology of the frustules and the original geometry of the pores are well preserved, this is confirmed by SEM and TEM techniques. The observed features of these diatomites match specifications of various industrial applications, such as catalyst supports, filtering aids and production of mesopores materials.

5. References