CHARACTERIZATION OF ESKISEHIR (TURKEY) SEPIOLITES

OKTAY BAYAT1, CEMALIE SIFLEK2, ZEHRA ALTINCELE3, and NIL YAPICI4

1Department of Mining Engineering, Çukurova University, Balcali, Adana, Turkey
2Aladag Technical College, Çukurova University, Adana, Turkey
3Department of Mining Engineering, Atatürk University, Erzurum, Turkey

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ABSTRACT

The mineralogical, morphological, physical and chemical properties of four different Turkish sepiolites were compared in this study. The mineral matter in the sepiolites, determined by means of X-ray diffraction, is dominated mainly by quartz and dolomite. Sepiolite was identified with the highest degree of crystallization at the peaks from 12.25 to 12.34 Å. All the sepiolite samples show low-calcium content. Based on size distribution results of all the samples, average grain size varies between 0.143 mm and 0.180 mm. SEM and TEM images results show fibrous morphologies.

Key words: Characterization, Crystallinity, Sepiolite, Scanning Electron Microscope, Thermal behaviour

INTRODUCTION

Sepiolite (Si$_2$O$_5$Mg$_x$(OH)$_y$(H$_2$O)$_z$,8H$_2$O), which is a magnesium silicate of fibrous morphology and a natural clay mineral, has a high surface area and nano-sized channels that contains water (Miura et al., 2012; Murray, 1999; Ozcan and Gok, 2012; Suarez and Garcia-Romero, 2012). Sepiolite crystal system is orthorhombic and the form is sub-microscopic. General structure of sepiolite contains magnesium ions that could be changed by iron, nickel, aluminium, and copper ions (Chuppina, 2008).

The general structure of sepiolite demonstrates an alternation of blocks and tunnels that grow in the fiber direction (Figure 1). Each block is composed of two tetrahedral silica sheets enclosing a central sheet of magnesium oxide-hydroxide (Alkan et al., 2005; Brauner and Preisinger, 1956; Okte and Sayinsoz, 2008; Vico, 2003).

Three types of active sorption sites are included in the sepiolite mineral structure (a) oxygen ions on the tetrahedral sheet of ribbons; (b) Mg ions coordinated to the water molecules; and (c) SiOH groups throughout the fiber axis (Lemic et al., 2005).

Sepiolite is preferred in various applications such as pharmaceuticals (Sugiuara et al., 1996), filters (Weir et al., 2001), catalyst supports (Aznar et al., 1996), absorbents (Kılışıoğlu and Aras, 2010; Rodriguez et al., 2010), pigments (Giustetto et al., 2011; Hubbard et al., 2003) and sepiolite-polymer sheets (Bokobza and El Bounia, 2008; Miura et al., 2012). Furthermore, because of the sepiolite high surface area (up to 300 m$^2$ g$^{-1}$), it is mostly used in oil refining waste water treatment; the removal of odour, drug, and pesticide carriers; paper and detergent; etc. (Hongxiang et al., 2006; Sabah and Celik, 2002).

Sepiolite is produced in Spain, Turkey, China and USA. China sepiolites, which contain bigger fractions of long fibers, provide benefits for producing composite materials with better mechanical qualities (Bellmann et al., 1997; Miura et al., 2012).

Intensive research has been carried out to determine the

![Figure 1. Schematic structure of a sepiolite (Soheilmoghaddam et al., 2014).](image-url)
characteristics of the natural Turkish sepiolites. A comparative study of four natural Turkish sepiolites, which represent 70–80% of the total production of Turkey supplied as raw material to industry from the studied region, was made with the aim of understanding the real variability of the properties in the sepiolite samples. For this purpose, four samples have been studied by X-Ray Fluorescence (XRF) spectrometer, X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR) and grain size distribution measurement.

MATERIALS AND METHODS

Materials

In this research, natural sepiolite samples from different sources and geological origins were sought to perform this study as seen in Table 1 and Figure 2. The samples were crushed, ground and wet sieved through a 0.063 mm size sieve before characterization analyses.

The material in grey colour from Sakarya Minerals Co. was named as SCN-1. The second sample (white colour), was from Dolsen Mining Co. and named as SCN-2. The samples taken from ÖzMaltaş Mining and Turan Mining Companies were also white in colour and named as SCN-3 and SCN-4 (Figure 3).

Characterization techniques

XRD

Mineralogical characterization was performed by X-ray diffraction (XRD) using a Shimadzu XRD-600 model diffractometer with Cu Kα radiation and a graphite monochromator. The test samples were powdered by hand in an agate mortar and the powders were scanned from 2 to 70° 2θ at a 0.05° 2θ/3 s scan speed to determine the mineralogy of the samples.

SEM

The particle morphology and textural relationship were established by scanning electron microscopy. SEM observations were performed using a JEOL JSM 6510LV microscope operating at 20 kV.

TEM

TEM observations were performed by depositing a drop of the diluted suspension on a microscopic grid with collodion. Images were obtained using a JEOL 2100F HRTEM microscope equipped with a double-tilt sample holder (up to a maximum of ±45°) at an acceleration voltage of 200 kV, with a 0.5 nm zeta-axis displacement and 0.31 nm point-to-point resolution.

XRF

The chemical composition of the sepiolites was determined by X-Ray Fluorescence (XRF) spectrometer using Panalytical B.V. MiniPal model equipment.

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**Table 1.** Sepiolite samples locations and location map

<table>
<thead>
<tr>
<th>Code</th>
<th>Company</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN-1</td>
<td>Sakarya Minerals Co.</td>
<td>Eskisehir, Beylikova, Yukarı-Dudas</td>
</tr>
<tr>
<td>SCN-2</td>
<td>Dolsen Mining Co.</td>
<td>Eskisehir, Sivrihisar, Yenidogan-Karacaören</td>
</tr>
<tr>
<td>SCN-3</td>
<td>ÖzMaltaş Mining</td>
<td>Eskisehir, Körpe</td>
</tr>
<tr>
<td>SCN-4</td>
<td>Turan Mining Company</td>
<td>Eskisehir, Sivrihisar, Kurtseyh</td>
</tr>
</tbody>
</table>

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**Fig. 2.** Location map showing the four main sepiolite districts and sample in the Eskisehir region of Turkey.
**FT-IR**

FT-IR analyses (450-4000 cm⁻¹) were recorded at room temperature with Perkin Elmer Spectrum one FT-IR spectrophotometer using KBr pellets to see functional groups of natural sepiolite.

**Sizing**

Grain size of samples was measured by Malvern Zeta-sizer Nano ZS-3600 equipment. Samples were added a drop of 0.25 M NaOH and then mixed with distilled water for 15 minutes. Then the mixes were stirred in the ultrasonic probe unit (severity level 20) for 10 minutes. After that, samples were sieved through 1 μm screen and measured by means of Malvern Nanosizer zs-3600 equipment.

**Surface Area**

A NOVA 2200 E model surface analyzer was used for determining specific surface areas of the samples corresponding N₂ adsorption–desorption isotherms. All samples were pre-treated and analyzed in the same way: 2.3 g of the raw sample, powdered in a manual mortar, were out-gassed for 2 h at room temperature and then 4 h at 110°C at a reduced pressure of 2 μm Hg. The isotherms were obtained following a previously fixed 40-points P/P₀ table and the reproducibility of isotherms was checked.

**RESULTS**

The samples studied were found to be pure or almost pure. Figure 4 shows the XRD patterns of the sepiolites. All XRD patterns of the studied samples present the reflections of sepiolite, but a detailed study of these patterns allows us to find some differences. Typical sepiolite characterized by a sharp and intense peak at 12.34 Å indicating the presence of well ordered sepiolite. For SCN-1 sample, sepiolite was identified with the highest degree of crystallization at 12.34 Å and 2.67 Å (7.18° and 33.52° 2θ). X-ray diffraction (XRD) analysis of SCN-1 sample indicates that sepiolite and quartz which is identified at 3.34 Å are the major components along with traces of dolomite (2.89 Å), feldspar (3.24 Å), hematite (1.67 Å) and illite (4.46 Å). Likewise, SCN-2 and SCN-3 samples were pure or almost pure.
show very similar results. The peaks of well crystallized sepiolite were identified at 12.25 Å (5.19° 20). XRD analysis of the SCN-2 sample results shows that calcite which is identified at 2.95 Å is the main trace component along with quartz (4.32 Å), feldspar (3.26 Å) and hematite (1.66 Å). Main trace components of SCN-3 are quartz (3.34 Å), illite (4.49 Å), feldspar (3.21 Å) and hematite (1.67 Å). However, the SCN-4 sample, which was taken from the Kurtseyh region, shows that sepiolite (12.32 Å) is the major component and feldspar (3.21 Å) along with quartz which is identified at 3.34 Å are the trace components. Also, no hematite or dolomite minerals were observed in the SCN-4 sample. The studied area is surrounded by hills consisting of Upper Cretaceous ultramafic rocks, partially surrounded by Upper Paleozoic dolomitic limestone, and covered by an alkaline and sulphate-bearing lake about 200 km long and 100 km wide from the Middle Miocene to Pliocene (Ece and Coban, 1994). Based on XRD studies, the sepiolite samples studied could be defined as dolomitic sepiolites.

All the images show fibrous morphologies. There were no significant differences in the SEM images of samples. Sepiolite fibrils were observed around 1–1.5 µm length in the sample of SCN-1 (Figure 5a). For SCN-2, crystallized sepiolite fibrils were also seen with a length of 1.5–2 µm coexisting with dolomite rhombs (Figure 5b). The sepiolite fibrils in dendritic and fibrous network structure with a length of approximately 0.5–1 µm were observed in SCN-3 (Figure 5c). Dolomite crystal formation was seen between the sepiolite fibrils. Evolving of some sepiolite fibrils was also observed over the dolomite crystal showing rhombs. As seen in Figure 5d, the crystallized sepiolite fibrils parallel to each other in 1.5–2 µm in length were seen coexisting with dolomite rhombs.

The textural features observed by electron microscopy (transmission-TEM) confirm that all of the samples studied present the characteristic fibrous morphology and can be seen in Figure 6. Although the samples can be differentially classified as macroscopic and clay sepiolites depending on the length of the fibers, all of them are nanometric in size with respect to the cross section of the fibers. Fibers can show lengths of less than 1 µm (Figure 6-B, C and D). However, there were no fiber forms on sepiolites from SCN-1.

The chemical composition of the sepiolite samples is presented in Table 2. The chemical analysis of SCN-1 sepiolite indicates that major components are SiO$_2$ (47.81%), MgO (10.90%), CaO (2.41%), Al$_2$O$_3$ (10.00%) and Fe$_2$O$_3$ (4.86%). Likewise, major components of the SCN-2 sample are SiO$_2$ (51.87%), MgO (23.00%) and CaO (1.59%). Chemical analyses of SCN-3 show abundant SiO$_2$ (44.41%) and MgO (19.90%) with subordinate CaO (3.08%) and Fe$_2$O$_3$ (1.90%). Furthermore, SiO$_2$ (59.94%), MgO (12.20%), Fe$_2$O$_3$ (0.74%) and CaO (0.38%) are the major components observed in SCN-4 sample.

![SEM images of the sepiolite samples.](image-url)
FTIR spectra of un-treated sepiolite samples are shown in Figure 7. All the samples show relatively similar results. The Mg,OH band at 3689–3427 cm⁻¹ characterized by weak bonding strength is ascribed to the presence of OH groups in the octahedral sheet and the OH stretching vibration in the external surface of sepiolite. However, between the 3427–1819 and 1659–1654 cm⁻¹ bands are respectively assigned to the OH stretching, representing the zeolitic water in the channels and bound water coordinated to magnesium in the octahedral sheet. The band at 1456–1440 cm⁻¹ developed due to the hydroxyl bending vibration again reflects the presence of bound water. The Si–O coordination bands at 1210–1019 and 987–981 cm⁻¹ represent the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet.

Based on zetasizer measurements, size distributions of the samples are not homogeneous. Therefore, the clusters consist of two different sizes. This situation can be clearly seen in the size distribution of the samples in Figures 8–9. Average grain size of samples was 0.143 mm, 0.145 mm, 0.159 mm and 0.180 mm for SCN-1, SCN-4, SCN-3 and SCN-2, respectively. Finesses of the sepiolite samples showed that they can be used as a reinforcing filler in rubbers and plastics, as natural rubber and PVC after surface modification with an organic compound. In literature (Galan, 1996), sepiolite has been extensively studied as a polymer filler and a pharmaceutical product. The exceptionally low values of these properties found in some samples cannot be related to the presence of impurities, but rather to their structural and textural features. Two types of microporosity that can be described are structural microporosity and interfiber microporosity. The SSA and the porosity of each sepiolite is the result of the sum of the intracrystalline or structural microporosity and the textural porosity (interfiber microporosity and mesoporosity). As a consequence, there is a hierarchical distribution of pore sizes, which is different for each sepiolite. The lowest values of microporosity are related to the presence of very open pores and the sepiolites with higher SSA are those having a smaller length and a more closed porosity. The sepiolites investigated in this study are very different from the point of view of their crystallinity, texture, porosity and SSA.

The values of the BET were 165.287 m²·g⁻¹, 102.725 m²·g⁻¹, 219.439 m²·g⁻¹ and 129.928 m²·g⁻¹ for SCN-1, SCN-2, SCN-3 and SCN-4, respectively. It demonstrates that there is a significant difference in the surface properties of this mineral.

### Table 2. Chemical analyses of the sepiolite samples. Percentage of major oxides

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>K₂O</th>
<th>MgO</th>
<th>Cr₂O₃</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>NiO</th>
<th>Rb₂O</th>
<th>SrO</th>
<th>ZnO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN-1</td>
<td>47.81</td>
<td>10.00</td>
<td>4.86</td>
<td>2.41</td>
<td>0.44</td>
<td>0.07</td>
<td>1.58</td>
<td>10.90</td>
<td>0.05</td>
<td>0.21</td>
<td>0.11</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>n.d.</td>
<td>21.10</td>
</tr>
<tr>
<td>SCN-2</td>
<td>51.87</td>
<td>2.37</td>
<td>0.75</td>
<td>1.59</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.10</td>
<td>23.00</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.07</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.22</td>
<td>n.d.</td>
<td>20.01</td>
</tr>
<tr>
<td>SCN-3</td>
<td>44.41</td>
<td>3.18</td>
<td>1.90</td>
<td>3.08</td>
<td>0.15</td>
<td>n.d.</td>
<td>0.42</td>
<td>19.90</td>
<td>0.15</td>
<td>n.d.</td>
<td>0.07</td>
<td>0.03</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.01</td>
<td>25.70</td>
</tr>
<tr>
<td>SCN-4</td>
<td>59.94</td>
<td>2.05</td>
<td>0.74</td>
<td>0.38</td>
<td>0.09</td>
<td>n.d.</td>
<td>0.41</td>
<td>12.20</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.57</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.01</td>
<td>0.01</td>
<td>23.30</td>
</tr>
</tbody>
</table>

*Lost on ignition, n.d. not determined.*
Fig. 7. FTIR spectra of the sepiolite samples.

Fig. 8. Size distribution (intensity) of the sepiolite samples.
With these high surface area properties, the sepiolite samples, especially SCN-3, can be used in paints, enamels, detergents, plastics, cements, adhesives, pesticides, etc. The behaviour of different sepiolite-filled rubbers with that of kaolin compared and found that the mechanical properties and ageing characteristics of the sepiolite rubbers to be similar or better than those of the kaolin-filled products (Gonzalez et al., 1981).

CONCLUSIONS

In this study, four different sepiolite samples were studied to determine the characteristics of the natural Turkish sepiolites. Major sepiolite beds lie beneath the gypsum series in the studied area (Eskisehir basin). The chemical analysis and XRD result of SCN-1, SCN-3 and SCN-4 samples, which were obtained respectively from near Eskisehir, Beylikova, Yukari-dudas, Körpe and Kurtsuy regions of Eskisehir, Turkey indicate that quartz is the main component. However, dolomite is the main component in SCN-2 obtained from near the Yenidogan and Karacaoren regions. Ecce and Coban (1994) stated that soluble Mg and Si with minor amounts of Al were supplied by the dissolution of ultrabasic rocks under alkaline conditions. Mg primarily came from the ophiolite complex and secondarily from the dissolution of dolomites. In addition to the primary silica source of diatomites, basic hydrothermal solution from underneath the paleolake along the fracture systems was the second major source of excess silica, which precipitated as lense-shaped opal beds overlying the organic matter rich sepiolite beds. Based on size distribution results of the samples, average grain size varies between 0.143 mm and 0.180 mm. All the SEM images results show fibrous morphologies. Sepiolite is indeed a potential natural clay mineral that can be conveniently used as absorbents, environmental deodorants, catalyst carriers, polyesters, asphalt coatings; paints, pharmaceutical uses, decolorizing agents, filter aids, anticing agents, phytosanitary carriers, cigarette filters, plastisols, rubber, animal nutrition, detergents, cosmetics, pet litter, agriculture (soil conditioning, fluid carriers for pre germinated seeds, seed coating; fertilizer suspensions) grease thickeners, NCR paper, drilling fluids. Since there is a huge deposit of sepiolite in Turkey, there is great potential for its utilization. Sepiolite mostly is used in making of decorative objects and as a pet litter in Turkey. The characterization results obtained represents a data in order to increase the usage area of sepiolite in Turkey. For this purpose, it is essential that we characterize the sepiolite samples.

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