SEM-EDX characterization of an iron-rich kaolinite clay

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Kaolin clay from Deopani deposit of Assam contains high amount of iron. Kaolinite particles, characterized by SEM-EDX, are pseudohexagonal and arranged in face-to-face pattern. Clay particles are coated with iron- and titanium-bearing minerals, which can be separated by wet high intensity magnetic separator Titaniferous impurities present as coatings on kaolinite particles are difficult to remove by oxalic acid treatment.

Keywords: Classification, Industrial minerals, Leaching, Magnetic separation, Particle morphology

Introduction
Kaolinite (white if pure) clay, one of the most versatile industrial minerals, is mostly used as ceramic raw material, coating and filler pigment for paper, filler for paint, rubber, insecticide etc., and also used in catalyst manufacture, in formulation of medicine, cosmetics, etc. Mined kaolin usually contains silica (as quartz) as major contaminant and Fe- and Ti-bearing minerals that impart colour as other contaminants. Kaolin occurs in Deopani of Karbi Anglong district, Assam, India. The deposit is estimated to contain 1.0 million tonnes of workable kaolinite. Physico-chemical characteristics of clay and its beneficiated products, using chemical, X-ray diffraction (XRD) and Fourier transform infra red (FTIR) analysis, have been reported. Fe content, chief colour imparting component of clay, could be reduced from 9.48% to about 1.00% by size separation (SS) and oxalic acid leaching (OAL) due to favourable Fe-mineralogical form (sideritic). Beneficiated fractions are suitable for using as ceramic raw material, filler material for paper, rubber, plastic, paint etc.

This paper reports characteristics and particle morphology of clay and its beneficiated products using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Materials and Methods
Kaolin clay was collected from exposed faces of Deopani deposit, located at 26°14'27" to 26°14'39" N latitudes, 93°45'05" to 93°46'05" E longitude and extend over an area of 0.0348 km² and 0.40 km² in block I and block II respectively. Thickness of deposits varies from 2.40-23.20 m (av 7.77 m) in block I and 0.95-7.60 m (av 2.99 m) in block II. Overburden (0-16.0 m) consists of soil, shale, limestone, sandstone and coal. Kaolinitization occurs in a lensoid pattern in granite body along NE-SW direction, which approx. coincides with foliation plan of granitic gneisses. Precambrian granites and granitic gneisses with different degrees of weathering dominate the area and are overlain by Tertiary sediments.

Representative clay samples were prepared from bulk clay following Indian standard method. Clay was suspended in water, stirred, and a fraction (~53 µm) was separated by sieving and further utilized for beneficiation by SS and OAL. A wet high intensity magnetic separator (WHIMS) was used to separate nonmagnetic and magnetic fractions of clay. Fe and Ti contents of samples were estimated by wet chemical analyses and X-ray fluorescence (XRF) methods. Mn content of clay was determined by following standard techniques.

SEM and EDX analysis were recorded by using LEO S430 scanning electron microscope coupled with energy dispersive X-ray analyzer model Oxford LINK ISIS. Samples were prepared by dispersing dry powder on double sided conductive adhesive tape. Samples were coated with carbon by arc discharge method for SEM-EDX. Samples were scanned in secondary electrons (SE) for morphology and back scattered electrons (BSE) mode for compositional image. Particles with white patches
Results and Discussion

Chemical analysis of crude clay sample, its –53 µm fraction and some other fractions show that Fe, Ti and Mn can be separated by SS, WHIMS treatment and OAL (Table 1). Table 2 shows Fe$_2$O$_3$ content of coarse (–53 µm +10 µm), medium (–10 µm +4 µm) and fine (–4 µm) fractions of as such clay and those obtained after leaching with 1M oxalic acid solution. Removal of iron from different size fractions of clay by oxalic acid treatment, as reported earlier, is presented in Fig. 1. XRD had shown that crude clay contains kaolinite and quartz as major mineral constituents, siderite as major iron bearing impurities along with small amounts of mica and goethite and/or hematite.

SE image of -53 µm fraction (as such) of clay (Fig. 2a) shows kaolinite particles of varying sizes that are arranged in face-to-face patterns. Some individual well crystalline pseudohexagonal edges of kaolinite as well as some rolled and rough edged kaolinite particles are also observed. Some kaolinite particles are below 1 µm size. Spongy quartz (Fig. 2a) might have resulted due to soil environment of Assam and particularly of Karbi Anglong district, which is acidic, hot moist subhumid and excessively drained. Hot and humid weathering environment also favours weathering of labile minerals to kaolin group minerals. Formation of sericitic mica type mineral, an intermediate between micas and clay minerals, are also possible. Some patches associated with wedge shaped minerals, which coat kaolinite particles as impurities, are also observed. Ti-bearing rock forming minerals associated with varying amounts of Fe and Mn form wedge shaped minerals. EDX spectrum of marked patches (Fig. 2b) shows presence of Fe and Ti along with minor amounts of Mn.

Among SE images of magnetic (Fig. 3) and nonmagnetic (Fig. 4) fractions of -53 µm clay, obtained by WHIMS treatment, magnetic portion showed presence of very high amount of patches (Fig. 3a). The fraction is rich in quartz and clay platelets, which are highly coated and stacked together. EDX analysis showed presence of

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>MnO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>LOI</th>
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</thead>
<tbody>
<tr>
<td>Crude clay</td>
<td>58.44</td>
<td>19.11</td>
<td>9.48</td>
<td>0.59</td>
<td>0.267</td>
<td>0.54</td>
<td>0.38</td>
<td>10.98</td>
</tr>
<tr>
<td>-53 µm fraction</td>
<td>47.20</td>
<td>35.75</td>
<td>2.86</td>
<td>0.90</td>
<td>0.022</td>
<td>0.17</td>
<td>-</td>
<td>12.23</td>
</tr>
<tr>
<td>-53 µm, nonmagnetic</td>
<td>45.04</td>
<td>38.67</td>
<td>1.10</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.65</td>
</tr>
<tr>
<td>-53 µm, magnetic</td>
<td>23.92</td>
<td>33.50</td>
<td>20.94</td>
<td>8.13</td>
<td>0.528</td>
<td>-</td>
<td>-</td>
<td>11.05</td>
</tr>
<tr>
<td>Fine fraction obtained*</td>
<td>45.35</td>
<td>38.31</td>
<td>1.01</td>
<td>0.57</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13.75</td>
</tr>
</tbody>
</table>

*Fe$_2$O$_3$: oxalic acid = 1.0: 0.4 mol ratio; Fine fraction: - 4 µm

<table>
<thead>
<tr>
<th>Fe$_2$O$_3$: oxalic acid (M)</th>
<th>Coarse</th>
<th>Medium</th>
<th>Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:0.0</td>
<td>3.38</td>
<td>2.52</td>
<td>2.21</td>
</tr>
<tr>
<td>1.0:0.4</td>
<td>2.60</td>
<td>1.53</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Coarse: - 53 µm + 10 µm; Medium: - 10 µm + 4 µm; Fine: - 4 µm

Table 1—Oxide composition (wt %) of Deopani kaolin and its beneficiated fractions

Table 2—Fe$_2$O$_3$ content of beneficiated fractions

Fig. 1—Removal of Fe from Deopani kaolin by oxalic acid (spot marked as Fe) were analyzed by EDX to ascertain presence of Fe and Ti.
very high amount of Fe, Ti and Mn in this fraction (Fig. 3b, Table 1). Kaolinite platelets are clearly visible in nonmagnetic fraction (Fig. 4a), which is comparatively free from patches. EDX spectrum (Fig. 4b) also shows very low Fe content. Although chemical analysis showed presence of Ti (Table 1), EDX pattern did not indicate presence of Ti-bearing minerals in nonmagnetic portion.

SE image of coarse fraction, separated from clay without acid leaching, shows presence of some large and spherical particles of quartz (Fig. 5a and b). Rounded nature of quartz particles and spherical grains indicate recycled nature and maturity of sediment accumulation. Quartz particle at higher magnification shows spongy surface and microcracks. One of the blocks shows exfoliation at one end, which may be attributed to presence
of sericitic mica. Stacks of kaolinite are also observed. Coarse fraction also shows patches, rich in Ti and Fe bearing minerals and containing traces of Mn as indicated by EDX pattern (Fig. 6), which coats quartz particles and stacks of kaolinite.

SE images of medium (Fig. 7) and fine fractions (Fig. 8) separated from clay without acid leaching show that kaolinite platelets have broken edges. Large kaolinite particles in medium fraction are coated with very fine particles, which are well-formed booklets of kaolinite layers. In fine fraction, some relatively big sized kaolinite particles are coated with patches containing wedge shaped titaniferrous minerals. EDX analysis shows that
Fig. 7—(a) SE image of medium fraction of unleached Deopani kaolin: kaolinite particles with broken edges (→); booklets of kaolinite (→); wedge shaped titaniferrous mineral (→). (b) EDX analysis (qualitative) of marked patch.

Fig. 8—(a) SE image of fine fraction of unleached Deopani kaolin. (b) EDX analysis (qualitative) of marked patch.

Fig. 9—(a) SE image of coarse fraction of acid leached Deopani kaolin. (b) EDX analysis (qualitative) of marked patch.
Fe, Ti and Mn contents of coatings decreases in order: coarse > medium > fine fraction (Figs 6-8).

SE image of coarse fraction contains large quartz particles with surfaces etched by acid solution, due to dissolution of Fe bearing minerals, exposing pores and channels. Amounts of patches in different fractions decrease in order of coarse (Fig. 9) > medium (Fig. 10) > fine (Fig. 11) fraction. It is less in acid treated fractions than corresponding untreated fractions. Patches are maximum in untreated coarse fraction (Fig. 5) and minimum in acid treated fine fraction (Fig. 11). Fe and Ti content of patches, revealed by EDX, follow same trend as with patches in these fractions (Figs 9-11). Untreated coarse fraction contains maximum Fe and Ti (Fig. 5) and acid treated fine fraction contain minimum amount of these impurities (Fig. 11). Removal of Fe by acid treatment is highest in fine fraction followed by medium and coarse fraction (Fig. 1). SEM-EDX investigation reveals that it is difficult to remove completely coatings of titaniferrous minerals from kaolinite particles.
Conclusions

SEM-EDX investigation shows that iron-rich kaolin from Deopani deposits of Assam, India contains pseudohexagonal kaolinite particles in face-to-face arrangement, quartz and titaniferrous minerals. A large amount of clay particles are coated with patches containing Fe, Ti and Mn. Highly coated particles can be separated as magnetic fraction by WHIMS treatment. Fe content of coatings decreases in the order: coarse > medium > fine fraction. SEM investigation indicates that amounts of patches in acid treated fractions are less than corresponding untreated fractions and it is minimum in acid treated fine fraction. EDX analysis also shows that Fe and Ti content of patches are less in acid leached fractions and are minimum in fine fraction of clay. Although, acid treatment considerably removes Fe and Ti bearing minerals, kaolinite particles still remains coated with it.

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References