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Physico-chemical Properties of Tunisian Bentonitic Clays

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Bentonites, which consist essentially of clay minerals belonging to the smectite group, have a wide range of chemical and industrial uses. The structure, chemical composition, exchangeable ion type and small crystal size of smectite are responsible for several properties, including a large chemically active surface area, a high cation exchange capacity and interlamellar surface having unusual hydration characteristics. Two samples collected from Gafsa and Kef deposits, are studied by some physico-chemical methods. Results of X-ray diffraction, chemical analysis, infrared spectroscopy, cation exchange capacities and specific and total surface confirm the general smectitic character of the collected samples.

INTRODUCTION

Smectite is the name used for a group of phyllosilicate mineral species, the most important of which are montmorillonite, beidillite, nontronite, saponite and hectorite. These and several other less common species are differentiated by variation in chemical composition involving substitutions of Al for Si in tetrahedral cation sites and Al for Fe, Mg and Li in octahedral cation sites. Smectite clays have a variable net charge which is balanced by Na, Ca, Mg and H adsorbed externally on inter-sheet surfaces.

The physico-chemical properties of smectite clay minerals determine their industrial utilisation. The main uses of smectite are in drilling muds, as a binder for foundry moulding sand and in palletising of iron ores, as a clarifying agent for oils and fats[1, 2], in agriculture, in civil engineering and in paints, pharmaceuticals and cosmetics[3].

The aim of the present work is to show how mineralogical and chemical examination data of collected sample clays may be used to indicate the suitability of clay for different applications.

EXPERIMENTAL

Two represented samples SG and SK (Aleg and El Haria formation) were collected from two bentonitic deposits near Gafsa and Kef. The clay fraction was

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purified by classical method[4], repeated cation exchange with 1 N NaCl solution, washing, sedimentation and dialysis.

The chemical analyses were obtained by using X-ray fluorescence. For X-ray diffraction studies, the diagrams were recorded with a Philips goniometer using the Kα1 radiation of copper. The infrared spectra were obtained by using either KBr pellets or self-supporting film (2 mg/cm^2) and were recorded with Perkin-Elmer 783 dispersive spectrometer from 4000–400 cm^{-1}. For some XRD and IR measurements, the samples were further exchanged with Na and Li. The cation exchange capacities (CEC's) were determined by the copper ethylene diamine method[5]. BET surface areas[6] were measured with a micrometric instrument. The interlamellar surface of purified sample was determined by the ethylene glycol method[7].

RESULTS AND DISCISSION

The results obtained by X-ray fluorescence are summarised in Table-1. The following preliminary points may be noticed:

(i) The total percentage of the analysed elements (in oxide form) is close to 100% for Na exchanged purified samples.
(ii) The two samples contain large amounts of iron.
(iii) The amounts of non-exchangeable potassium suggest the presence of illite.

TABLE-1
CHEMICAL ANALYSIS OF THE CRUDE AND Na EXCHANGED PURIFIED SAMPLES

Oxide	Aleg sample		El Haria sample	
	SG crude	SG Na	SK crude	SK Na
SiO_2	35.00	50.00	53.80	50.00
Al_2O_3	15.93	16.98	10.80	13.00
Fe_2O_3	9.47	9.50	7.87	9.50
MgO	1.41	1.94	8.70	8.70
Na_2O	2.76	2.23	0.11	2.70
K_2O	1.36	1.31	0.84	0.50
CaO	1.91	0.38	2.93	0.70
Ignition loss (%)		17.57		15.00

The number of cations per unit cell of the purified samples were calculated by Mauguin's method. The structural formulas of the two purified samples are:

$Na_{0.66}K_{0.26}Ca_{0.06}(Si_{7.48}Al_{0.52})(Al_{2.47}Fe_{1.07}Mg_{0.43})O_{20}(OH)_4$ for SG Na

and

$Na_{0.76}K_{0.09}Ca_{0.11}(Si_{7.80}Al_{0.70})(Al_{1.54}Fe_{1.04}Mg_{0.189})O_{20}(OH)_4$ for SK Na

X-ray diffraction: The nature of the impurities was determined by examining the crude samples (Figs. 1 and 2). Quartz (reflection at 3.35 Å) and calcite (reflection at 3.03 Å) are the major impurities. The positions of 001 reflections of the smectite appear at 15.5 Å for the two samples suggesting that the fraction might be in the Ca exchange form[8]. The purified samples with Na exchange show the position of the 001 reflection (d = 12.6 Å) characteristic of a sodium smectite or vermiculite or an interstratified sample of these minerals with illite. Heating the sample in air above 500°C collapses the interlayer spacing to 10 Å. Treatment with ethylene glycol (shifts the 001 reflection to 1.71 Å) confirms the presence of smectite or interstratified illite-smectite (a vermiculite would have its 001 reflection at 14 Å). The position of 002 reflection is very sensitive to smectite-illite interstratification[9]. It goes from 8.46 Å for pure smectite to 10 Å for pure illite. Our glycolated samples show 002 reflection appear at 8.84 Å for SG

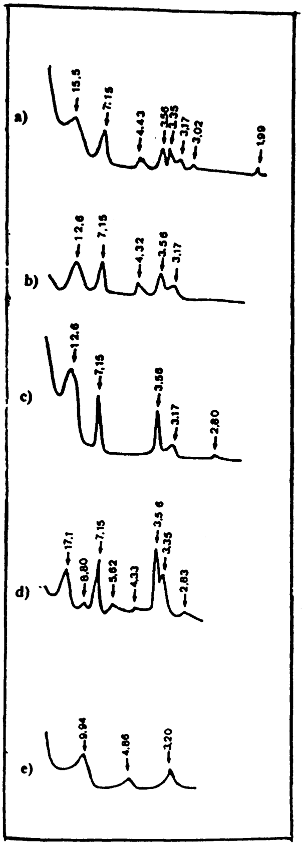

Fig. 1. X-ray diffractograms of SG sample: (a) crude powder (b) Na exchanged powder (c) oriented Na exchange film (d) oriented Na exchange and glycolated film (e) oriented Na exchanged and heated at 500°C film.

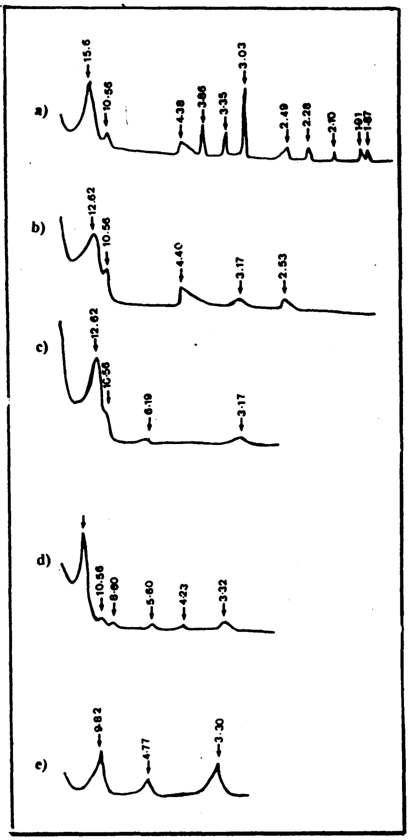

Fig. 2. X-ray diffractograms of SK sample: (a) crude powder (b) Na excahnged powder (c) oriented Na excahange film (d) oriented Na exchange and glycolated film (e) oriented Na exchanged and heated at 500°C film.

purified sample and 8.6 Å for SK purified sample indicating the irregular interstratification of SG and SK samples. Without 001 reflections of smectite, the diffractogram of SG purified sample shows the 001 and 002 reflection of kaolinite at 7.15 and 3.56 Å. These reflections disappear after heating at 500°C. Small amounts of palygorskite (reflection 001 at 10.56 Å) appear in SK sample diffractogram.

The mineralogical compositions of crude and purified samples obtained by X-ray diffraction are given in Table-2.

TABLE-2
MINERALOGICAL COMPOSITION (%) OF CLAY DEPOSITS

Sample	Smectite	Kaolinite	Palygorskite	Calcite	Quartz
SG crude	53	30	0	7	10
SK crude	75	n.d.	4	18	3
SK purified fraction	93	n.d.	7	n.d.	n.d.
SG purified fraction	78	22	n.d.	n.d.	n.d.

n.d.: not-detected

Infrared spectra: Fig. 3 shows the infrared spectra of SG Na and SK Na samples over the frequency range of 4000–400 cm^{-1}.

(i) The distinct increase of infrared absorbency at 3620 and 915 cm^{-1} confirms the dominant presence of dioctahedral smectite with (Al, Al—OH) stretching and bending bands.[10]

(ii) The absorption bands at 3420 and 1625 cm^{-1} and the OH frequencies for the water molecule adsorbed on the clay surface.

(iii) Bands at 880 cm^{-1}, 835 cm^{-1} and 800 cm^{-1} can be assigned to [[Fe, Al—OH], [Mg, Al—OH] and [Mg, Fe—OH]][11].

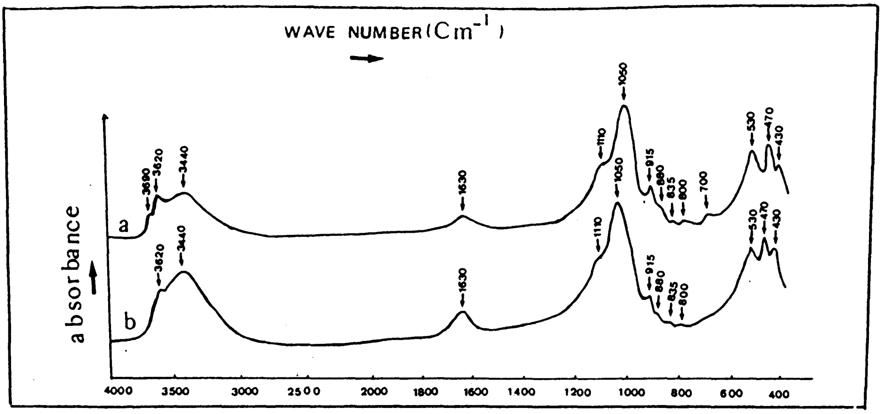

Fig. 3. Infrared spectra of purified samples: (a) SG Na (b) SK Na

(iv) The (Si—O) bands are strongly in the silicate structure and can be readily recognised in the infrared spectrum by the very strong absorption bands in the 1100–1000 cm^{-1} region. The substitution Al for Si in the silicon-oxygen lattice modifies (Si—O) vibrations and cause new absorption band to appear at 530 cm^{-1} for (Si—O—Al) in the 600–400 cm^{-1} region[12].

(v) The infrared absorption properties of kaolinite are established at frequencies 3685 cm^{-1} and 700 cm^{-1}. That is the lone difference between the SG Na and SK Na samples infrared spectra.

Cation exchange capacities, S_{BET} and total surface: The cation exchange capacities of crude and Na exchange samples and S_{BET} and total surface of purified samples are given in Table-3. After purification the cation exchange capacities increase. The high amount of kaolinite seems to explain the low values of cation exchange capacities and total surface of SG sample.

TABLE-3
CATION EXCHANGE CAPACITIES, S_{BET} AND TOTAL SURFACE OF SG AND SK SAMPLES

Sample	CEC (meq/100 g of cacined clay)		S_{BET} m^2/g	Total surface (m^2/g)
	Crude	Na exchange	Na exchange	Na exchange
SK	78	95	52	750
SG	56	65	83	528

Distinction between Montmorillonitic and Beidellitic Fractions

Montmorillonite and beidillite are also distinguished by X-ray diffraction using Greene Kelly test,[13]. This depends on the observation that Li saturated montmorillonite (octahedral substitution) collapses irreversibly when heated to 220°C for 24 h, whereas beidellite (tetrahedral substitution) similarly heated does not effect any changes.

The recommended procedure is as follows. The Li saturated material, which may conveniently consist of an oriented flake, is heated to 220°C overnight. It is saturated with ethylene glycol and X-ray diagrams are recorded. A 001 spacing about 9.6 Å indicates montmorillonite, one of 17.1 Å indicates beidillite. In fact, both reflections were observed, indicating that both octahedral and tetrahedral substitutions are present and suggest that the mineral is of an intermediate composition (Fig. 4). The 001 spacing at 9.6 Å reveals that lithium ions migrate from the interlayer positions to the vacant octahedral sites by thermal treatment. The consequence is a decrease of exchangeability of interlamellar cations. The ratio of the octahedral and tetrahedral substitution was quantitatively determined from the cation exchange capacities before and after lithium migration (Table-4).

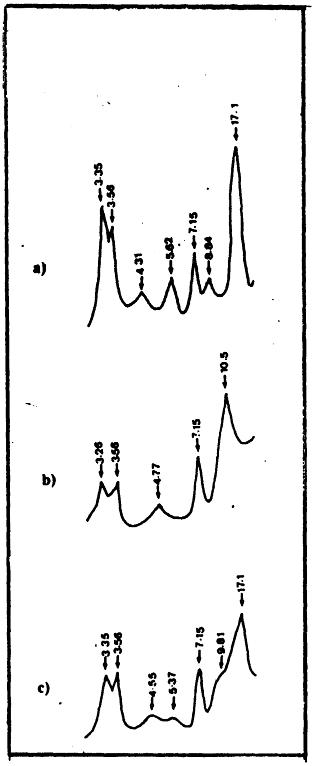

Fig. 4. X-ray diffractograms of oriented Li exchanged SG sample: (a) glycolated (b) heated at 220°C for 24 h (c) glycolated after heat treatment at 220°C for 24 h

TABLE-4

ESTIMATION OF TETRAHEDRAL AND OCTAHEDRAL SUBSTITUTIONS BY CATION EXCHANGE CAPACITIES OF Li-EXCHANGED SAMPLES

	SG sample	SK sample
CEC of Li exchanged sample	66	94
CEC of heated Li exchanged sample	35	53
% of tetrahedral substitution	53	56
% of octahedral substitution	47	44

(CEC: meq/100 g of calcined clay)

The infrared spectrum is another tool to detect the lithium migration in the octahedral sheet. The infrared spectrum (Fig. 5) of Li exchange in unheated SK sample is similar to that of the Na sample. However, after heating at 220°C in vacuum, three new bands appear at 935, 855 and 810 cm^{-1} which could be characteristic of bending frequencies in the environments AlAlLiOH, MgAlLiOH and MgFeLiOH respectively[14]. The residual intensity of AlAlOH vibration at 915

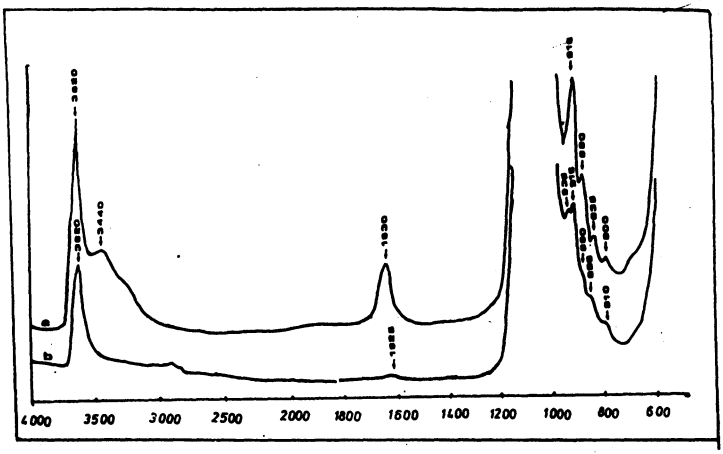

Fig. 5. Infrared spectra of Li$^+$ exchanged SK sample: (a) air dried room temperature and (b) dried at 220°C in vacuum.

cm^{-1} and of the FeAlOH vibration at 880 cm^{-1} after heating suggests that a fraction of the Li does not migrate in octahedral sheet.

Conclusion

The crude samples are an irregular interstratified illite-smectite. The smectitic fraction on the interstratified phase is always larger than 50%. More than half of substitutions are of tetrahedral origin, confirming again the beidellitic character of the samples.

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