Associated Minerals and their Influence on the Optical Properties of Jordanian Kaolin

Akl M. Awwad*, Rafat Ahmad, Hatem Alsyouri

Industrial Chemistry Centre, Royal Scientific Society, Amman, Jordan

Abstract

Kaolin samples from Al-Disi kaolin deposits in southeastern region of Jordan are associated with mineral impurities, which impart color to this kaolin and adversely affect its application in paper and paint industries. The associated mineral impurities with kaolin were separated by deflocculating of kaolin particles in polymeric sodium polyphosphate solution. The crude kaolin, deflocculated kaolin (suspended kaolin), and the associated mineral impurities with kaolin (residue) were determined by X-ray fluorescence, X-ray diffraction, FTIR spectroscopy, and spectroscopic studies. The composition of the residue separated from Al-Disi kaolin composed mainly from quartz, feldspar, and hematite. The separation of these associated mineral impurities from al-Disi kaolin by deflocculating process improves the brightness of kaolin to be suitable for processing to produce kaolin that meets specifications for paper making, filler, cosmetics and other uses that demand high whiteness and low impurity content.

1. Introduction

Kaolin is a geologic term refering to a rock that is predominately composed of > 50% [1] of the mineral kaolinite $[Al_2Si_2O_5 (OH)_4]$. Kaolin is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral. The mineral kaolin is usually associated with various impurities: quartz, anatase, rutile, pyrite, siderite, feldspar, etc., depending on the origin and depositional environment [2]. These impurities affect the characteristic properties of kaolin and its utility for applications. The industrial applications of kaolin in ceramics tiles and glass, paper coating, rubber, adhesives, sealants, as filler [3] lead to an extensive research to be carried out on the nature of the existing impurities associated with kaolin [5-7]. In Jordan, although kaolin deposits occur, their industrial usage has been restricted to the manufacturing of ceramics. No research has been conducted to understand the genesis and suitable industrial applications of kaolin occurrences in the country.

Suspensions of kaolin particles in aqueous solutions are tremendously important in ceramics, pharmaceuticals, paints, and cosmetics industries. The performance of kaolin suspensions depends on the stability of these suspensions. The stability of the kaolin suspensions is governed by two factors van der Waals forces and repulsive electrostatic forces. kaolin suspensions are prepared by suspending the kaolin particles in aqueous solutions of different deflocculated agents such as sodium sulfite, sodium nitrate, sodium phosphate, monomeric and oligomeric phosphates [5,9-11].

The purpose of the present paper is to separate and identify the associated mineral impurities with kaolin by deflocculating of kaolin particles in sodium polyphosphate solutions and to be useful for industrial applications.

2. Materials and Methods

Kaolin clay samples have been collected from the quarry of Al-Disi district of Aqaba state located 45 km east of Al-Quweira town. The location of this site is shown in Fig.1. The mine area is around 54 Mt as given in the survey of Natural Resources authority, Jordan.

Clay samples in this study were crushed ground, using a vibrating Disc mill (model RS 200, Retsch-Germany). The clay was then sieved through a 325-mesh sieve (44 µm particle size) and washed with dionized water three times to dissolve soluble salts.

Concentration of associated minerals was performed by the following method: 100 grams of the fine powder of Al-Disi clay , 1-2 grams of sodium polyphosphate, and 200-400 ml of water were mixed in a glass tank and slurried by stirring with an electric stirrer for 30 minutes to form suspension of clay. The clay deflocculated particles were removed by decantation and repeated washing with water to get the associated mineral impurities concentrate as residue. The residue was dried in an oven at 105 ºC.
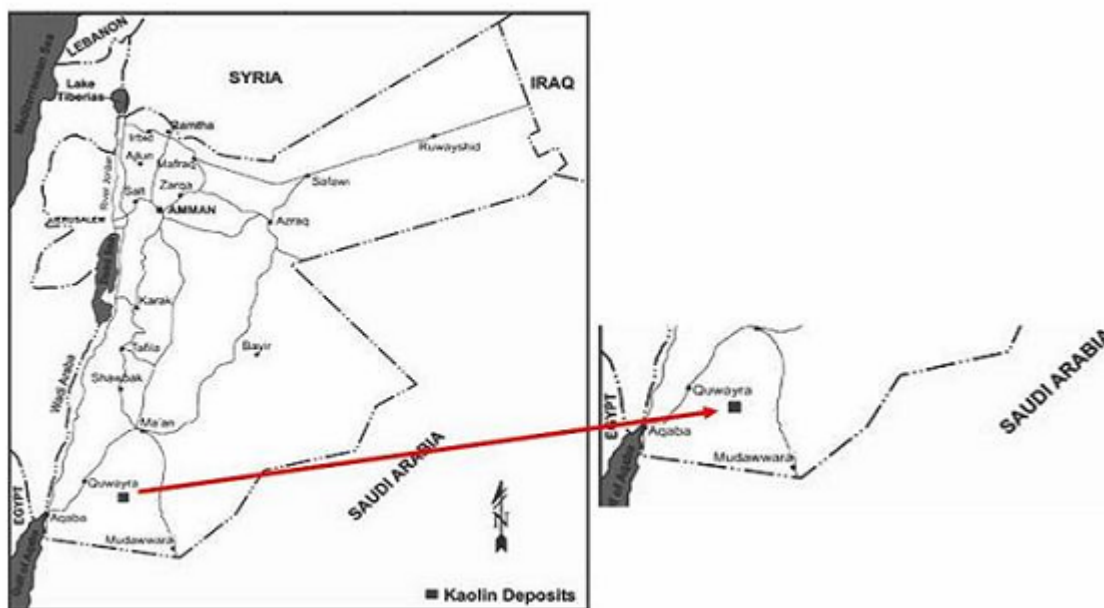
---

* Corresponding author. aklm@rss.gov.jo

Figure1. Location map of the kaolin mines in Jordan.■, Al-Disi deposits of kaolin

The chemical composition of the samples was determined by X-ray fluorescence (XRF-800 Shimadizu).

The XRD patterns were taken using X-ray diffractometer (Shimadzu XRD-6000) equipped with Cu Kα radiation source using Ni as filter and at a setting of 30 kV/30 mA. All XRD data were collected under the same experimental conditions, in the angular range $3^o \leq 2\theta \leq 50^o$.

FTIR spectra were obtained by IRprestige-21 Shimaduz FT-IR- spectrophotometer, using KBr pellet method.

Optical brightness and color values were measured by Color Touch Macbeth color-eye 7000 spectrophotometer. Brightness represents the percent of reflectance of light at a wavelength of 457 nm. The "Lab" system based on the color opposites gives representation of the colors. The term "L" is a measure of lightness/darkness and varies from 100 for perfect white to 0 for absolute black. The red/green color is indicated by "a". The more positive value a indicates reddishness and negative value indicates greenishness. Similarly, the yellow/blue shades are represented by "b", positive value for yellow and negative for bluishness.

3. Results and Discussion

Table 1 shows the chemical composition of the crude clay, the suspended clay and the concentrated associated minerals (residue) determined by X-ray fluorescence (XRF).

Table 1. Chemical composition of crude kaolin, suspended kaolin, and associated minerals in weight percent (nd = not determined).

	Crude kaolin	Suspended kaolin	Associated minerals
SiO_2	59.18	63.48	90.51
Al_2O_3	26.22	22.89	5.16
Fe_2O_3	1.52	1.36	3.05
TiO_2	1.42	1.33	nd
CaO	0.11	0.18	0.11
MgO	0.09	0.17	nd
Na_2O	0.11	0.09	0.08
K_2O	1.12	1.42	1.44
P_2O_5	0.11	0.18	nd
LOI	10.21	8.88	

It is observed that the concentrations of SiO_2 are greater than the theoretical value, which can be explained by the presence of various amounts of quartz in all samples as indicated by X-ray diffraction. After Si, the most abundant impurity elements are Fe, Ti, and K. Crude clay and suspended clay contain around 1.5% iron oxide and titanium oxide. It can be seen that the associated mineral impurities with clay predominantly composed of > 90% SiO_2, > 5% Al_2O_3, and > 3% Fe_2O_3.

The amounts of associated mineral impurities with clay in all samples studied   are 4% to 6% of the total crude clay. Also it can be seen in Table 1 that the ignition loss is less significant as compared to the theoretical value, which confirms the low carbonate in the clay samples. The K_2O percentage is more important. This gives an indication of the existence of illite and K-feldspar in this clay.

X-ray diffraction study (XRD) of the crude kaolin samples Fig. 2a showed that the kaolinite is the dominant mineral phase with quartz impurities. The suspended kaolin samples deflocculated by sodium polyphosphate Fig.2b show the emergence of a small peak at $2\Theta = 8.9$ relative to illite, which does not appear in the crude clay, this peak is too small to be detected in the crude clay samples. The associated mineral impurities are separated as residue by deflocculating process of crude kaolin as can be seen in Fig. 2C shows that quartz is the dominant mineral impurities with additional reflection of feldspar and hematite.
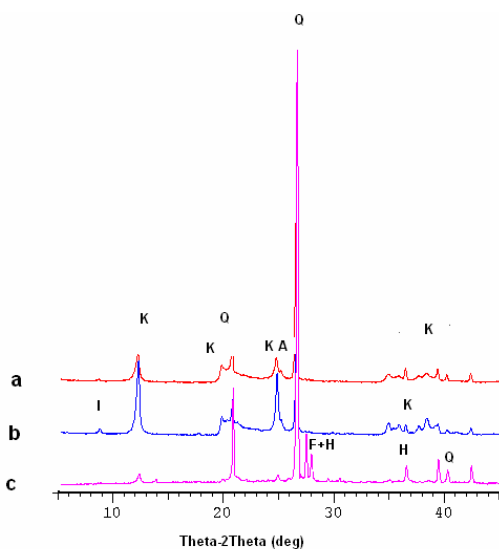
Figure 2. X-ray diffraction patterns of < 50-µm size (a) crude kaolin; (b) suspended kaolin; (c) associated mineral (residue). K: Kaolinite, Q: Quartz, A: Anatase, I: Illite,   F: Feldspar, H: Hematite.

FTIR spectra of the crude kaolin, suspended kaolin, and the residue (associated mineral impurities) are illustrated in Fig. 3. The FTIR profiles of both crude kaolin and the suspended kaolin are roughly similar, as seen in Figures 3a and 3b. The FTIR spectrum shows the strongest absorbance bands at 3698, 3655, 3624, 1040, 799, cm^{-1}, characteristic of kaolinite, Table 2.

A shoulder at $\approx$ 1099 cm^{-1} indicates the presence of quartz. A weak band at around 1449 cm^{-1} indicates the presence of carbonate bearing minerals. FTIR spectra of the residue Fig. 3c shows a strong band of H_2O at 3445 cm^{-1} dominates the OH-stretching region. The absorption bands in the 450 -1103 cm^{-1} owing to Si-0, Si-O-Si, Al-O-Si deformation and Si-0 stretching are characteristic of quartz and feldspar.

Table 2. FTIR band assignments of crude kaolin, suspended kaolin, and associated minerals.

Assignments	Crude/suspended kaolin Band (cm^{-1})	Associated Minerals Band (cm^{-1})
OH - vibration	3697, 3655, 3624	
OH stretching of water	3444	3444
OH deformation of water	1639	1647
CO_3 vibration	1449	1432
Si-O-Si	1098	1100
- Si-O-	1039	
AlAlOH	918	
Si-O-Si	795	800
Si-O stretching of quartz	758	
Al-O-Si	696	640
Si-O	649	
Si-O-Si deformation	538	
Si-O-Si deformation	471	475
Si-O deformation	430	

The microscopic studies showed that the associated minerals (residue) separated from Al-Disi kaolin clay by deflocculated kaolin in sodium polyphosphate consist mainly of Quartz, feldspar, and hematite, Fig.4.

The associated mineral impurities (residue) are treated with concentrated hydrochloric acid; a pale yellow solution is formed. The pale yellow solution was separated from the unreacted residue by filtration and analyzed by Inductively-coupled Plasma optical Emission Spectroscopy (ICP-OES). The results showed that the solution consists mainly of iron oxides. This result indicates the presence of small amounts of hematite in the residue. The microscopic photograph, Fig. 5 shows the remaining residue contains quartz and feldspar.

The data for the two optical properties whiteness and color values are reported in Table 3.

The whiteness of the suspended kaolin is compared to the crude kaolin sample of 49%. The term L is a measure of lightness/darkness and varies from 100 for perfect white to 0 for absolute black. The red/green balance is indicated by "a" (the more positive the value "a", the greater the redness and the more negative the more greenness). The yellow/blue shades are presented by "b". The positive value gives yellowness and the negative corresponds to blueness). The whiteness and color values such as Lab values in Table 3 show the whiteness of suspended kaolin (deflocculated by polymeric sodium polyphosphate); and are superior to that crude kaolin. Both kaolin samples have positive values for **"a"** and **"b"** indicating that they are red and yellow. The suspended kaolin sample have lower values of **"a"** and **"b"** than that of crude kaolin. This indicates that the redness and yellowness of suspended kaolin is decreased due to the decrease of metal oxides impurities such as iron oxides. It seems that these oxides decrease the whiteness of kaolin.
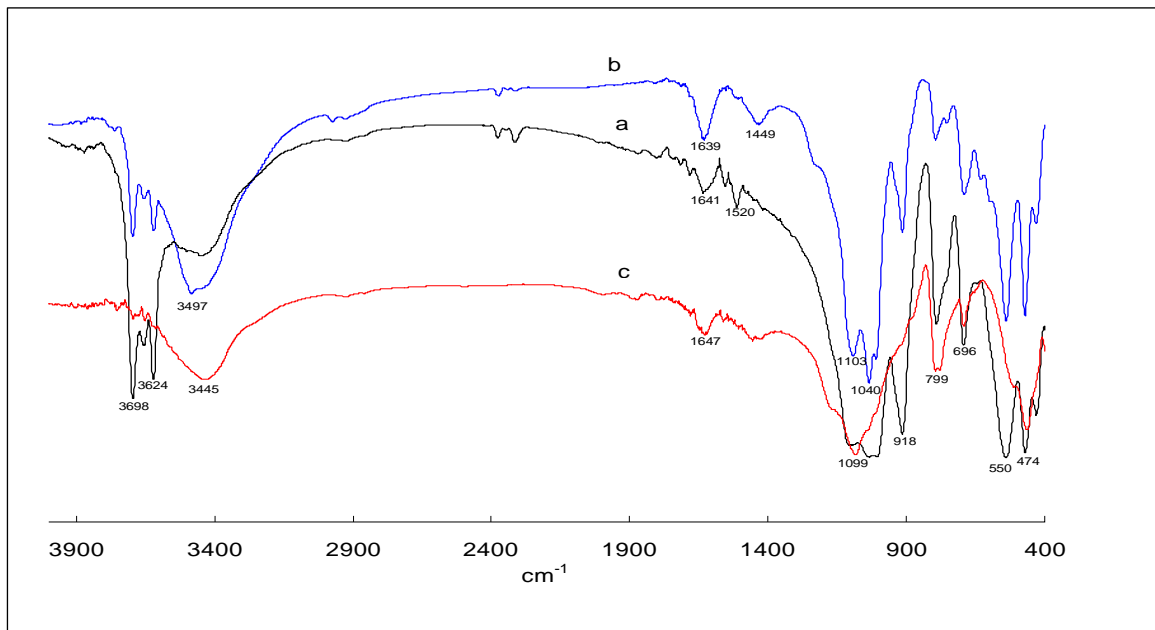
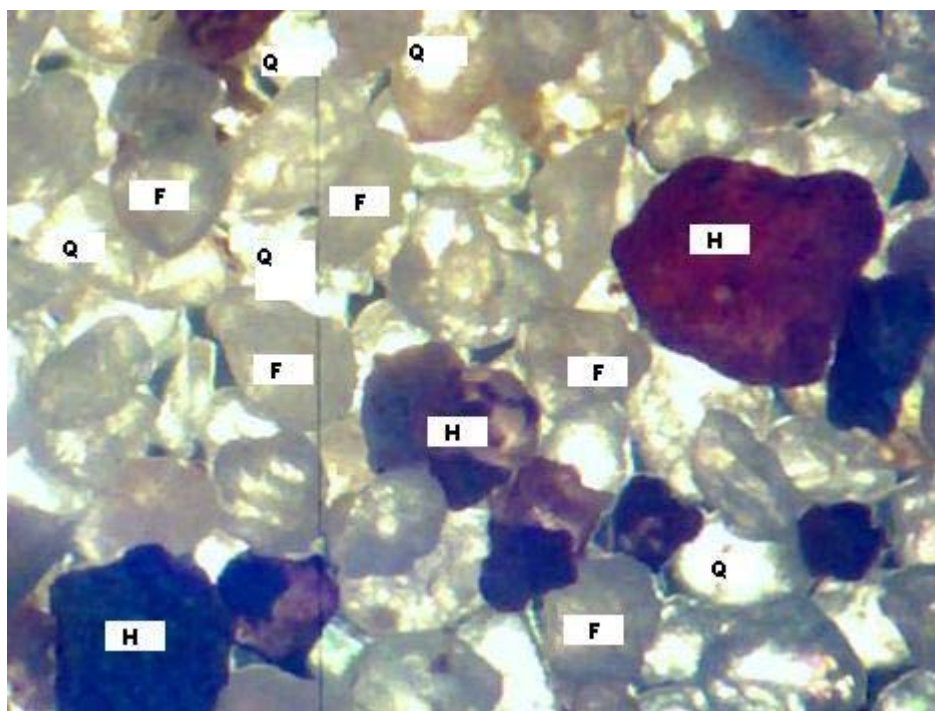Figure 3. FTIR spectra: (a) crude kaolin; (b) suspended kaolin; (c) associated minerals (residue).

Figure 4. Microscope pictures of associated mineral impurities taken by Wraymer BM-3400 T microscope with magnification x 200. H: hematite; F: feldspar; Q: quartz.
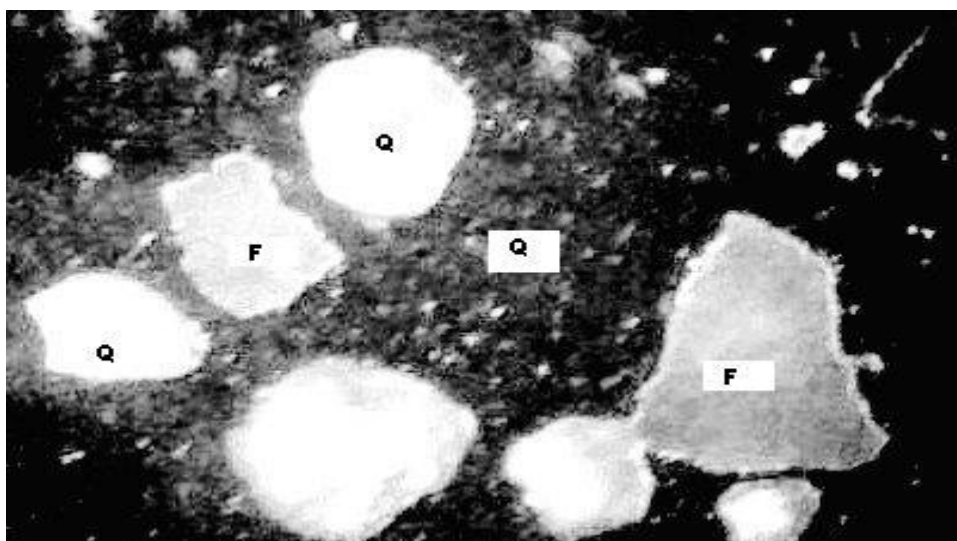
Figure 5. Microscope pictures of associated mineral impurities taken by Wraymer BM-3400 T microscope with magnification x 200. After treatment with hydrochloric acid. F: feldspar; Q: quartz.

Table 3. Optical properties: whiteness and Lab values of crude kaolin and suspended kaolin.

		Crude kaolin	Suspended kaolin
whiteness		49.17	65.27
color values	L	79.64	88.29
	a	2.29	0.69
	b	7.62	7.39

a: Reddishness value, b: Yellowness value, L: Lightness/darkness

4. Conclusion

The chemical analysis, XRF, and XRD show that Al-Disi kaolin clay is mainly constituted of silica and alumina in major quantities and iron, titanium, calcium, magnesium and other elements in minor quantities. The loss of ignition value indicates that clay has lower carbonaceous matter. The X-Ray diffraction study shows the presence of quartz, feldspar, hematite, and illite as major phases. The presence of the above minerals was further confirmed by microscopic studies. The deflocculating of kaolin clay with polymeric sodium polyphosphate (SPP-kaolinite clay) raised its whiteness from 49.17 to 65.27. The FTIR spectra analysis reveals that the polymeric sodium polyphosphate was basically held onto kaolinite clay.

Acknowledgments

References

[1] T. Dombrowsky, The orgins of kaolinite-implcation for utilization. In: Carty, W. (Ed.), Science of Whiteware. The American Ceramic Society, Westerville, OH, 2000, pp. 3-12.

[2] R.W.Grimshaw, Physics and Chemistry of Clay, 4th ed. Ernest Benn, London, ISBN: 1971, 0510-47701-7.

[3] H.H. Murray, Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition. VCH Publishers, 1986, pp. 109-136.

[4] W. B. Jepson, Structural iron in kaolinities and in associated ancillary minerals. In: Stucki, J. W.; Goodman, B. A.; Schwertmann, U. (Eds.), Iron in Soils and Clay Minerals. NATO Advanced Science Institutes Series. D. Riedel Publishing Company, Dordrecht, Holland, 1988, pp. 467-536.

[5] N. Yildiz, M. Erol, B. Baran, Y. Sarikaya, A. Calimil, Modification of rheology and permeability of Turkish ceramic clays using sodium silicate. Applied Clay Science Vol. 13, 1988, 65-77.

[6] S. Chandrasekhar, S. Ramaswamy, Influence of mineral impurities on the properties of kaolin and its thermally treated products. Applied Clay Science Vol. 21, 2002, 133-142.

[7] S. Chandraschar, S. Ramaswamy, Investigation on a gray kaolin from south east India. Applied Clay Science Vol. 37, 2007, 32-46.

[8] T. Manfredini, G.C. Pellacani, P. Pozzi, A.B. Corradi, Monomeric and oligomeric phosphate as deflocculants of concentrated aqueous clay suspensions.   Applied Clay Science Vol. 5, 1990, 193-201.

[9] D. Penner, G. Lagaly, Influence of anions on the rheological properties of clay mineral dispersion. Applied Clay Science Vol. 19, 2001, 131-142.

[10] F. Andreola, E. Castellini, J.M.F. Ferreira, S. Olhero, M. Romagnoli, Effect sodium hexametaphosphate and ageing on the rehelogical behaviour of kaolin dispersions. Applied Clay Science Vol. 31, 2006, 56-64.

[11] D. Derrington, M. Hart, T.M. White worth, Low head sodium phosphate and nitrate hyperfiltration through thin kaolinite and smectite layers- Application of   engineered systems. Applied Clay Science Vol. 33, 2006, 52-58.