

Possibility of Recoating of Impurities on Product Kaolin during Froth Flotation – HRTEM-EDS Study

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Abstract

Attempts were made to remove the Fe, Ti minerals from Gujarat kaolin by SC-HGMS and ultraflotation to improve the optical properties. The removal of Fe was higher by SC-HGMS, but that of Ti was almost the same by both techniques. The Fe content of the products was relatively low, but the brightness was lower than the expected. A drastic improvement in brightness was observed for the SC-HGMS product compared to the ultra flotation product. One of the probable reasons for the low enhancement in brightness by flotation was thought to be recoating of the impurities on the clay surface during flotation. XPS study conducted on the flotation product ruled out the possibility of such a coating. HRTEM-EDS analyses showed that most of the titania is present in the form of anatase particles of very small size. A part of the Fe forms independent particles of goethite /hematite having nano size. Rest of the Fe is found to be closer to anatase or kaolinite particles either as a part of the structure or nano sized independent particles adhering to the surface and hence is not easily separated. The ultra fine grains of Fe stained anatase remaining in the kaolinite surface after flotation is found to have a strong pigment effect. During flotation, high shear energy is given for dispersion and conditioning which is possibly reducing the particle size to submicron / nano level. The dissatisfying brightness of the flotation product is attributed to the presence of these fine / colloidal impurities. Fe content in the product samples is relatively low and its influence on brightness is probably smaller than that of the Fe stained anatase. The organic matter and ferriferous smectite identified in the sample even at small percentages may also have a pigment effect due to their dark color and colloidal distribution.

Keywords: kaolin, titaniferous minerals, HRTEM –EDS, ultra flotation, brightness

INTRODUCTION

Kaolin or china clay is a naturally occurring white material containing “kaolinite” $[Al_2Si_2O_5(OH)_4]$ as the major mineral. For most of the industrial applications, kaolin is to be beneficiated for removing the ancillary minerals such as quartz, ferruginous, carbonaceous, micaceous and titaniferous impurities [Jepson, 1988]. One of the highest value additions is achieved when the product kaolin meets the specifications of paint and paper coating grades where the critical properties are high brightness, low color values and small particle size [Murray, 1986 and Murray,1993]. The optical properties (brightness, **Lab** color, Hunter whiteness and yellowness) are improved only when the coloring impurities are removed. Even though the international specification for coating clays prescribes a value of $\geq 85\%$ brightness (ISO), higher brightness and low color values always fetch better price.

The present paper is a part of our investigation on the value addition of china clay from Mamuara mines of Gujarat. Our earlier studies on some Indian clays showed that the brightness is not directly related to the analytical Fe_2O_3 content in the clay which is contributed by “free” and “structural” types of Fe. On the other hand, it is influenced by the “Fe species” [Chandrasekhar, 1995, Chandrasekhar and Raghavan, 1999 and Chandrasekhar and Ramaswamy, 2002]. The main coloring impurity in Mamuara clay is found to be titaniferrous mineral especially in the ultrafine size range. The impurities were separated by super conducting high gradient magnetic separation (SC-HGMS), ultraflotation and both in combination. SC-HGMS improved the optical properties drastically whereas the improvement was marginal by ultraflotation. However, the brightness improvement did not match with the quantity of titaniferrous impurities removed during flotation. One of the reasons for this mismatch was thought to be a possible recoating of the impurities on the product clay surface during flotation. An attempt has been made to investigate this problem by studying the various samples derived from the clay by X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM) in combination with micro chemical analysis.

EXPERIMENTAL

Materials & Methods

The ROM clay was collected from the Mamuara mines in Kutch district of Gujarat and subjected to size classification by screening and small diameter hydrocycloning. The final product of size classification (the overflow solids of 10mm hydrocyclone) was subjected to SC-HGMS and ultraflotation separately and in combination. The products and the reject materials of these two operations were selected for the investigation. An XPS study was conducted on the ultraflotation product sample at Fraunhofer Institut Fertigungstechnik Materialforschung, Bremen with an XPS system VG (Typ 220i-XL). The four samples (1) SC-HGMS product (2) Ultra flotation product (3) Magnetic rejects and (4) Flotation rejects were analyzed by HRTEM at the Univ. of Geigswald, Germany. The chemical analysis of the feed and product samples was carried out following standard procedures [Bennett, 1971]. The optical properties were measured by Colortouch (ISO) Brightnessmeter, Technidyne Corporation, US.

RESULTS & DISCUSSION

Iron can be present in kaolin as “free” iron compounds like oxides, hydroxides, oxy-hydroxides, carbonates, sulphides etc. or as “structural” present in the framework of kaolinite or ancillary minerals like anatase, mica etc. The optical properties of kaolin are mostly dependent on the quantity and type of Fe minerals in kaolin. Our earlier work showed that Mamuara clay with 0.43% Fe_2O_3 and 1.61% TiO_2 has only 73% brightness whereas china clay from Thonnakkal (Kerala state) with 0.40% Fe_2O_3 and 0.5% TiO_2 has 85% brightness. Thus the total analytical iron content cannot be directly

Table 1: Properties of the Beneficiated Products From Mamuara Kaolin

Properties	FSCP	FSC-HGMSP	FSC-UFP	FSC-HGMS -UFP
% Fe_2O_3	0.37	0.29	0.38	0.24
% TiO_2	1.61	1.1	1.15	0.74
Brightness	73.1	83.4	76.0	84.3
L	90.33	94.68	91.81	94.8
a	0.61	-0.29	0.50	-0.16
b	6.06	4.85	5.63	4.53
HW	50.32	64.4	54.78	65.31
HY	9.58	6.92	8.75	6.83

FSCP – Final size classified product; HGMSP – High gradient magnetic separation product; UFP – Ultra flotation product

correlated to the brightness and it is the species of Fe which is of prime importance. It has been established that Mamuara clay is found to have “free” and “structural” iron as oxides/hydroxides and Fe stained anatase respectively. It is difficult to distinguish Fe stained anatase from anatase since both give X-ray reflection intensity at 3.52 Å. Large quantities of titaniferous minerals considerably reduce the brightness of the clay. Table 1 gives the Fe and Ti content in the beneficiated products of Mamuara clay and their optical properties.

The schematic representation of the removal of Fe₂O₃ and TiO₂ and brightness improvement in the size classified product of Mamuara clay is given in Fig.1. Ultra flotation is more selective to TiO₂ removal whereas SC-HGMS can easily remove paramagnetic and feebly magnetic iron and titanium minerals. SC-HGMS removes ~33 % of Fe₂O₃ and ~32 % of TiO₂ from the feed sample and the brightness improvement is ~10.3 units ISO. Ultra flotation of the feed clay sample removes ~12 % Fe₂O₃ and ~29 % TiO₂ with a brightness increase of only 3 units. When the SC-HGMS product clay is subjected to ultra flotation, another 12% Fe₂O₃ and 22% TiO₂ are removed and the brightness is enhanced by another 1.2 units. Here in these two cases of ultra flotation, the Fe removed may be essentially corresponding to the titaniferous minerals.

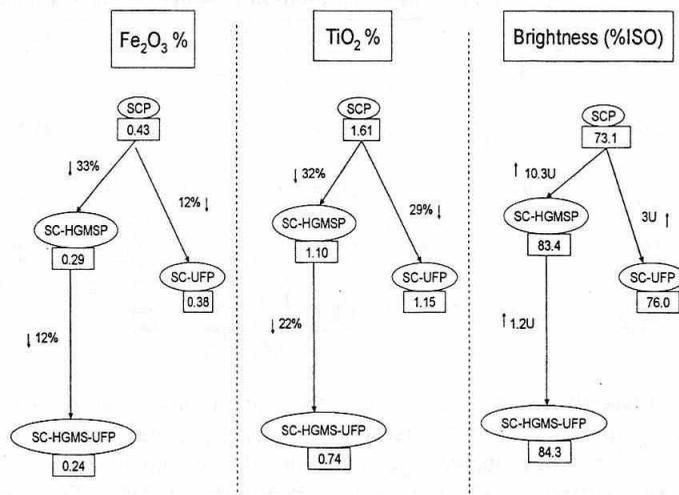


Fig. 1: Schematic Representation of Fe₂O₃ & TiO₂ Removal and Brightness Improvement in Mamuara Clay. SC - Size Classified ; HGMS - High Gradient Magnetic Separation ; UF - Ultra Flotation ; P - Product

Brightness is the percentage reflectance of light at a wavelength of 457 nm whereas whiteness relates better to people’s visual assessment. 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 the value of *a*, the greater the reddishness and the more negative the more greenishness). The yellow/blue shade is represented by *b* (the positive value gives yellowness and the negative to bluishness). Hunter whiteness (HW) and Hunter yellowness (HY) have the advantage of being single number quantities that are based on the entire visible spectrum. There is an increase of 15 units in whiteness corresponding to 11 units in brightness. The improvement in *Lab* values is much less in the ultra flotation product compared to the HGMS product indicating that less quantity of the colored impurities are removed by the former technique.

These results show that the brightness improvement is not linearly related to the removal of Fe₂O₃ and TiO₂. It is observed that SC-HGMS and ultra flotation remove almost same amount of TiO₂ whereas the former removes more of the Fe₂O₃ which includes the free iron also. Less improvement in brightness by flotation suggests that ferruginous minerals are not removed significantly which is more

deleterious than the titaniferous impurity. Free iron minerals are easily removable by SC-HGMS and once most of it is removed, the product on further ultra flotation gives only marginal improvement in brightness in spite of the considerable removal of TiO₂. The very small % of Fe remaining in the sample may be corresponding to the Fe stained anatase which has tremendous coloring effect on the white kaolin. This anomalous behaviour or mismatch may be due to the recoating of coloring impurity on the flotation product clay causing less brightness than expected.

XPS Study

The flotation product sample was subjected to XPS analysis. Table 2 gives the details. The measurement was done up to 200nm thickness on the sample. No iron could be detected on the surface until sputtering was done up to a depth of 180 nm. No difference could be found out in the Ti concentration from the surface to that thickness level. These results rule out the possibility of any coating on the clay particle surface. Perhaps, the structure and or morphology of the clay and / or the impurity particles may be undergoing some changes during the ultraflotation process which may be influencing the scattering of light / brightness of the product.

Table 2: XPS Analysis Data of the Ultraflotation Product (At % of Elements)

Sample	C	O	Al	Si	Na	Mg	Ti	N	Fe
Kaolin sample	43.8	39.1	9.1	7.31	0.3	0.2	0.1	-	-
After 1 min. sputtering	36.4	41.9	11.0	0.4	<0.1	-	0.1	-	-
After 10 min. sputtering	25.3	48.6	14.7	10.9	-	-	0.2	0.3	-
After 30 min. sputtering	19.6	51.8	15.9	11.9	-	-	0.2	0.7	<0.1
After 60 min.sputtering	15.4	52.3	16.5	14.7	-	-	0.2	0.8	<0.1

HRTEM Study

The TEM investigation has given information about the size and morphology of various particles and also about the presence of other constituents such as NaCl, gypsum, carbon etc. which were not identified earlier. The microprobe analysis gave the detailed chemical assay of selected particles. Micro analytically, the particles are grouped as kaolinite, anatase, Fe particles, crandallite-woodhouseite and "other particles". In the Figures 2, 3, 4, 5 and 6, the points of analysis are marked on the photographs by means of letters and the exact location of analysis is marked with an arrow. The elemental compositions are calculated from the EDS spectra of each particle.

Kaolinite

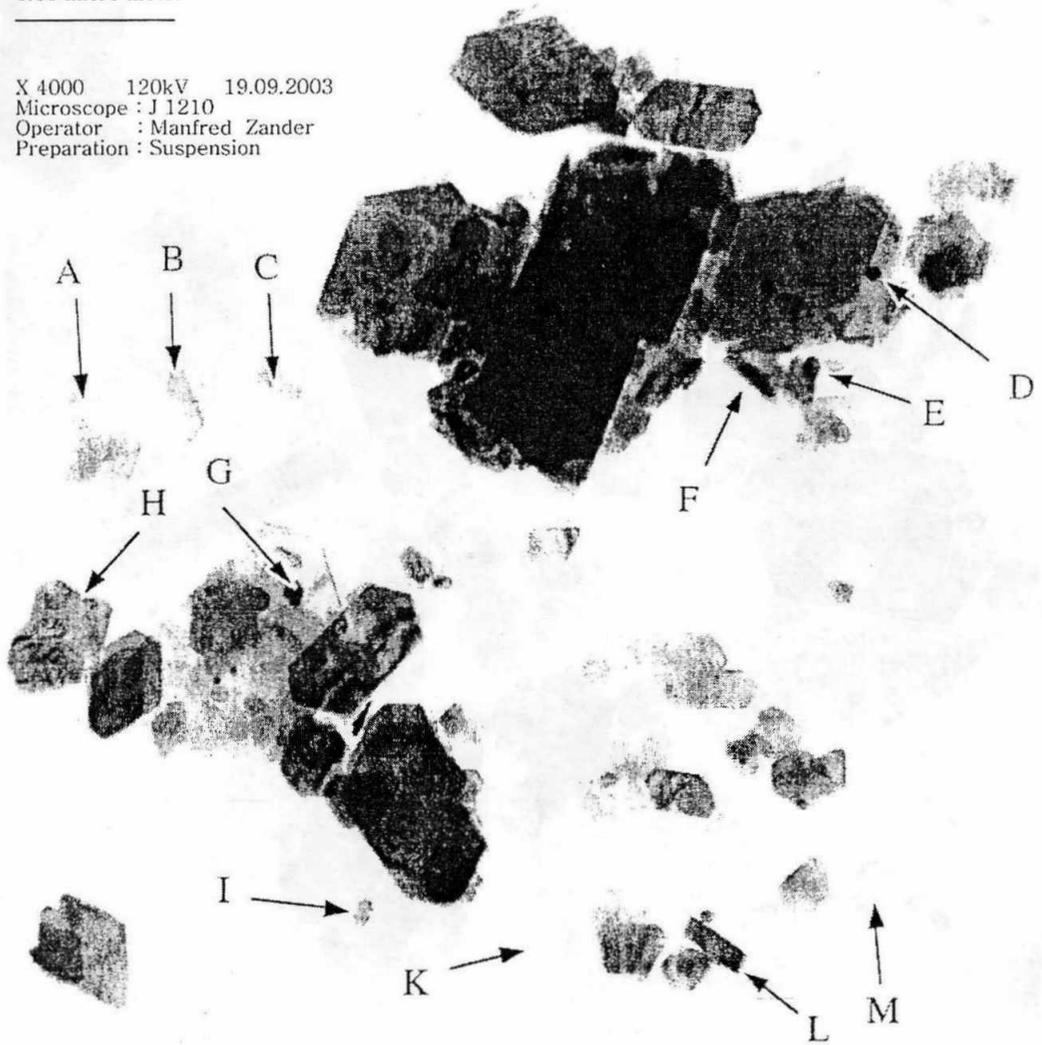
The TEM pictures show that the kaolinite builds well formed pseudo hexagonal leaflets or larger particles of crystallographic intergrowths of primary hexagonal tablets (particles A,B,C,F,H,K & M in Fig.2; D,E,H & K in Fig. 3, A,B,C,G,H & K in Fig. 4 and B, F & G in Fig. 5). The microanalyses of 73 small kaolinite crystals showed low Fe contents of 0.00 to 0.6% by weight. Only 9 analyses gave Fe contents > 0.6 % (maximum 1.9 %). It may be possible that the Fe is present in the kaolinite structure or as independent goethite or hematite particles fixed in a colloidal dimension within the small kaolinite structure or their intergrowths. In such a case, they will not show the TEM picture due to insufficient mass density.

Anatase

The titaniferous particles are anatase as confirmed by the XRD studies (reflections at 3.52 and 1.89Å). In almost all the TEM pictures, the anatase is visible in the form of xenomorphic particles much smaller than the kaolinite particles. The smaller granules are mostly round to oblong in shape

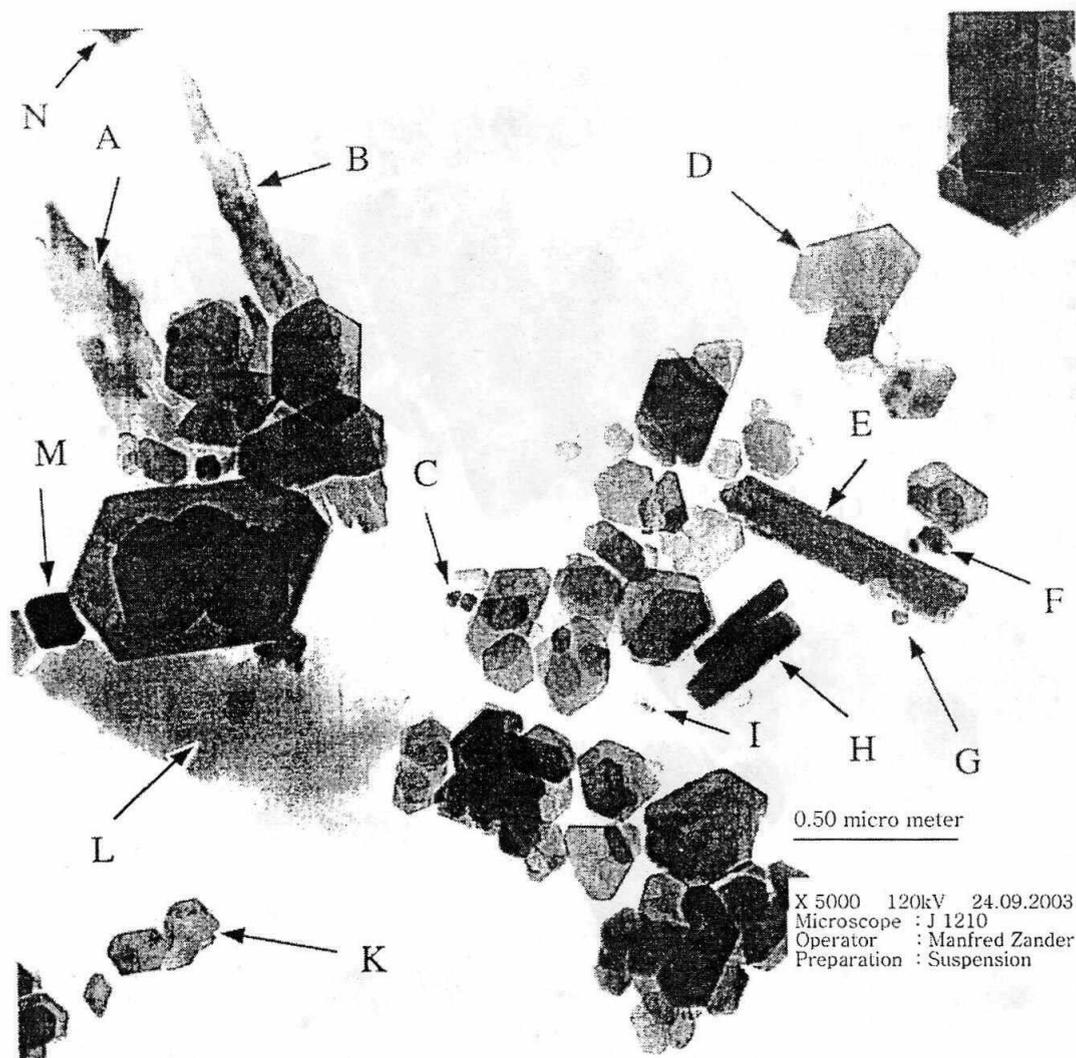
0.60 micro meter

X 4000 120kV 19.09.2003
 Microscope : J 1210
 Operator : Manfred Zander
 Preparation : Suspension



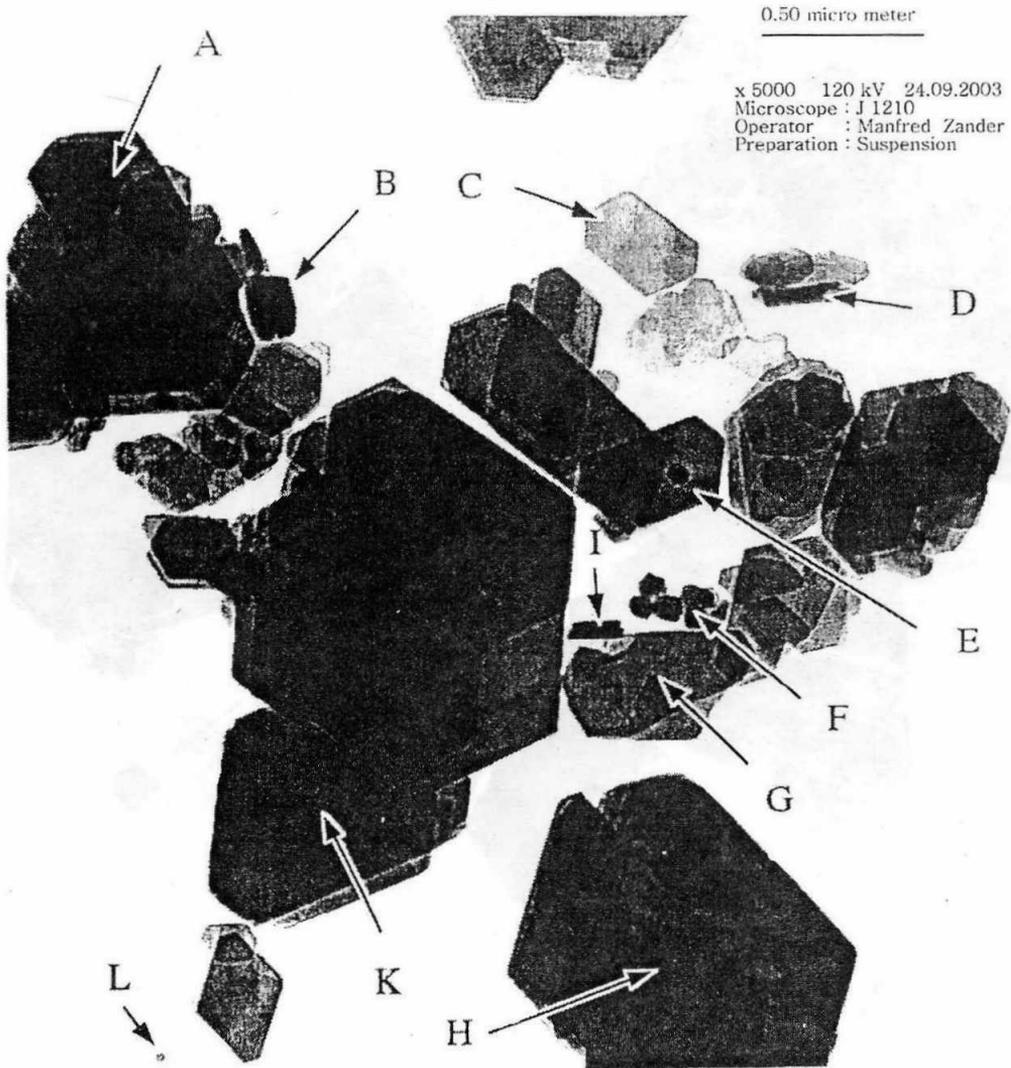
	S02A	B	C	D	E	F	G	H	I	K	L	M
	K	K	K	K/Ti	K/Ti	K	Ti	K	Ti	K	K/Ti	K
O	50.1	50.2	49.2	47.2	43.1	48.0	38.6	49.9	36.2	49.6	47.9	52.7
Si	24.4	24.4	25.1	23.0	14.4	26.3	6.2	25.9	0.4	25.4	19.8	24.3
Al	22.6	24.0	23.6	22.5	13.9	24.7	7.2	23.5	0.3	23.5	18.2	22.2
Ti	0.0	0.0	0.0	6.2	26.7	0.1	45.2	0.0	59.1	0.0	13.0	0.1
Fe	0.3	0.1	1.0	0.4	1.0	0.5	2.3	0.0	2.6	0.5	0.4	0.4
Mg	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca	0.1	0.1	0.2	0.0	0.0	0.2	0.0	0.0	0.4	0.0	0.2	0.0
K	0.0	0.2	0.2	0.3	0.2	0.1	0.4	0.2	0.2	0.4	0.3	0.2
Na	0.2	0.3	0.2	0.3	0.2	0.0	0.0	0.2	0.1	0.4	0.0	0.0
S	0.0	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
Cl	0.1	0.2	0.2	0.1	0.3	0.2	0.0	0.1	0.0	0.1	0.1	0.2
P	0.2	0.2	0.1	0.0	0.2	0.0	0.2	0.2	0.4	0.4	0.2	0.0

Fig. 2: HRSTEM Data of SC-HGMSP of Mamuara Clay



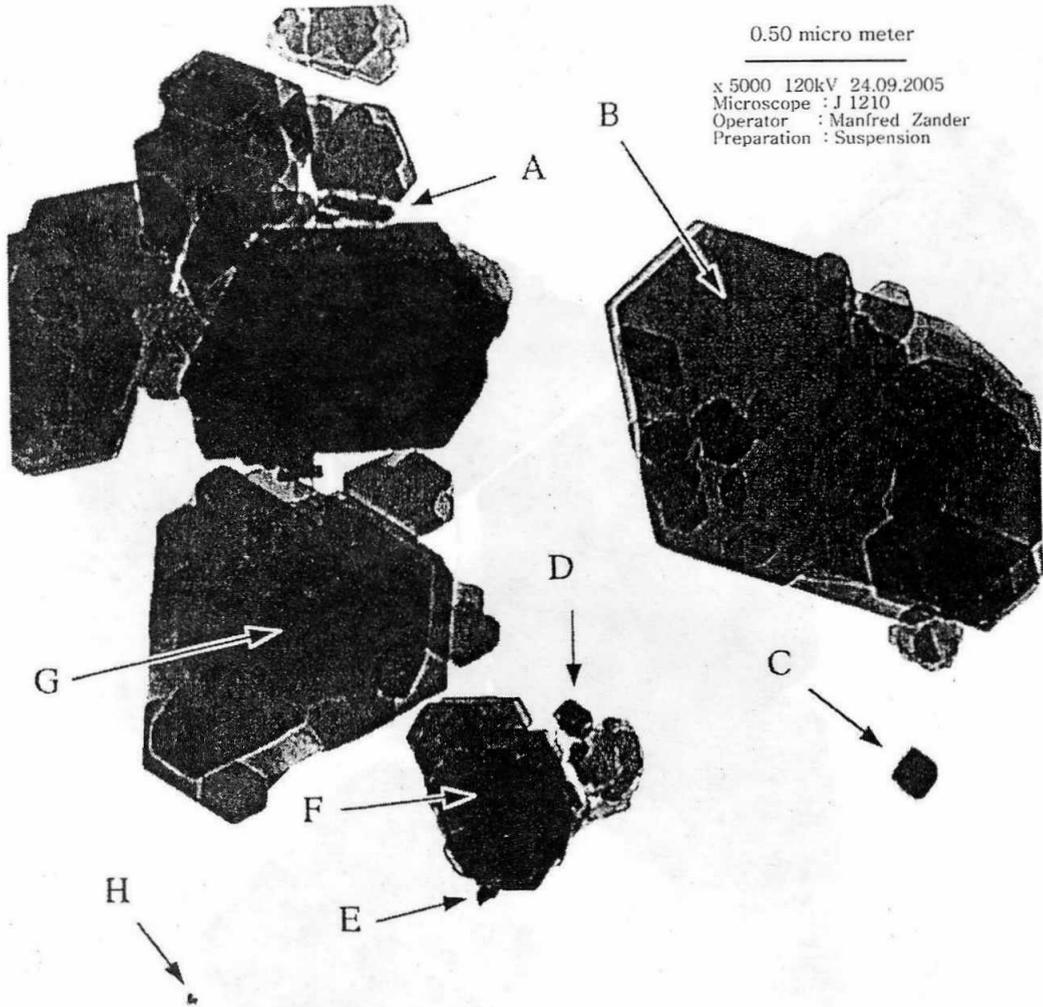
	103A	B	C	D	E	F	G	H	I	K	L	M	N
	Sa	Sa	Ti	K	K	Ti	Ti	K	Ti	K	Sa	Ti	Ti
O	28,5	23,8	41,8	50,9	50,8	36,7	34,5	49,9	37,8	50,9	26,1	40,1	50,9
Si	3,5	2,6	7,5	24,9	24,9	1,0	1,7	25,9	9,3	24,9	3,4	0,6	1,8
Al	1,5	0,8	5,7	23,5	23,0	1,0	0,9	23,4	1,2	21,5	2,8	1,2	2,0
Ti	0,0	0,0	39,0	0,0	0,0	57,4	55,5	0,0	22,6	0,0	0,0	53,2	55,6
Fe	1,4	0,7	2,1	0,0	0,1	1,7	4,0	0,1	5,9	0,4	0,8	1,9	1,6
Mg	0,2	0,0	0,2	0,1	0,9	0,0	0,0	0,0	1,2	0,4	0,9	0,6	0,1
Ca	44,9	39,5	0,2	0,0	0,2	0,4	0,0	0,0	0,7	0,0	0,9	0,1	0,0
K	7,3	16,8	1,1	0,1	0,4	0,2	0,1	0,1	4,3	0,2	11,9	0,0	0,0
Na	1,8	10,5	1,4	0,0	0,3	1,0	1,9	0,2	7,5	0,2	25,3	0,7	0,5
S	9,5	4,7	0,3	0,0	0,0	0,0	0,6	0,1	1,3	0,8	1,4	0,2	0,0
Cl	0,8	1,2	0,8	0,2	0,5	0,3	0,9	0,0	2,8	0,4	26,1	0,1	0,0
P	0,6	0,0	0,7	0,2	0,0	0,2	0,0	0,0	1,1	0,6	0,4	0,5	0,4

Fig. 3: HRSTEM Data of Flotation Rejects



	S01A	B	C	D	E	F	G	H	I	K	L
	K	K	K	K	K/Ti	Ti	K	K	K	K	Fe
O	51.3	49.8	52.7	51.5	44.6	34.4	50.9	51.4	47.9	53.5	
Si	24.5	24.3	23.7	24.2	15.0	1.1	25.4	24.3	25.2	24.0	
Al	23.6	24.3	22.4	23.2	11.5	0.8	22.9	23.5	24.0	22.0	
Ti	0.0	0.3	0.1	0.1	26.7	59.6	0.1	0.0	0.0	0.1	
Fe	0.2	0.3	0.4	0.7	1.4	1.9	0.1	0.1	1.4	0.2	+
Mg	0.0	0.0	0.2	0.1	0.2	0.3	0.0	0.2	0.5	0.0	
Ca	0.1	0.2	0.1	0.1	0.1	0.8	0.0	0.0	0.3	0.1	
K	0.0	0.2	0.2	0.0	0.3	0.3	0.1	0.1	0.2	0.0	
Na	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	
S	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	
Cl	0.2	0.5	0.3	0.2	0.3	0.1	0.2	0.0	0.1	0.1	
P	0.2	0.0	0.0	0.0	0.1	0.6	0.4	0.4	0.2	0.1	

Fig. 4: HRSTEM Data of Flotation Product

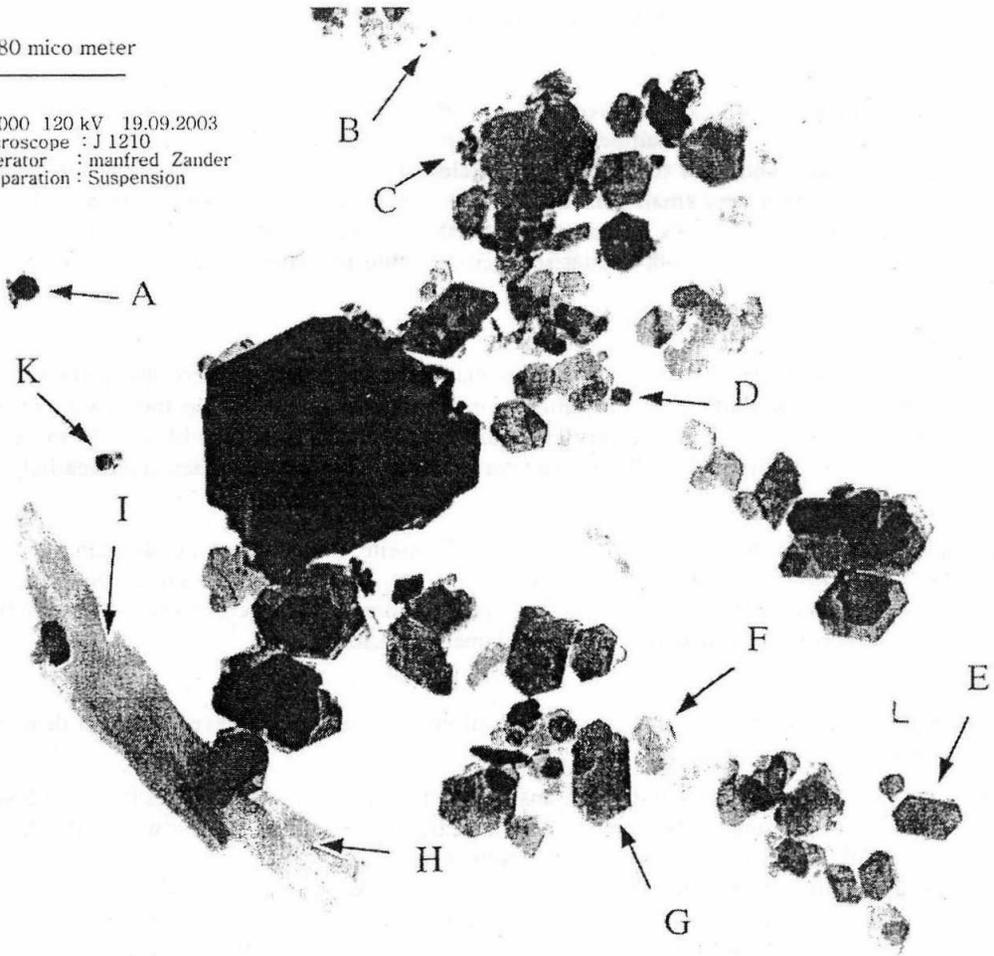


	S03A	B	C	D	E	F	G	H
	K	K	Cr*	Ti	K/Ti	K	K	Si
O	49,5	50,5	43,7	37,4	49,9	49,5	52,9	
Si	26,0	25,5	1,5	1,8	23,2	25,3	23,8	+
Al	23,8	23,0	21,7	1,9	21,7	24,0	22,6	
Ti	0,1	0,0	0,0	56,0	2,8	0,1	0,0	
Fe	0,2	0,3	0,3	2,1	1,7	0,7	0,2	
Mg	0,2	0,3	0,1	0,4	0,2	0,0	0,3	
Ca	0,0	0,1	0,8	0,1	0,2	0,1	0,1	
K	0,0	0,2	0,0	0,2	0,0	0,1	0,0	
Na	0,0	0,0	0,1	0,3	0,0	0,0	0,0	
S	0,0	0,0	2,8	0,0	0,0	0,3	0,0	
Cl	0,3	0,2	0,0	0,0	0,2	0,0	0,2	
P	0,0	0,0	13,4	0,0	0,1	0,0	0,0	
Sr*			3,9					
Ce+La*			11,7					

Fig. 5: HRSTEM Data of Flotation Project

0.80 micro meter

x 3000 120 kV 19.09.2003
 Microscope : J 1210
 Operator : manfred Zander
 Preparation : Suspension



	S02A	B	C	D	E	F	G	H	I	K	L
	Ti	Sa	Sa	Ti	K	K	K	Gi	Gi	Ti	Ti
O	37,3	9,4	18,2	38,3	51,7	50,2	50,6	29,9	32,4	34,3	39,1
Si	3,8	2,7	5,6	1,5	24,5	24,4	25,0	1,8	2,3	0,6	1,0
Al	4,5	0,1	4,3	2,2	22,0	21,5	22,6	0,6	1,1	0,9	1,4
Ti	51,4	0,2	0,0	53,4	0,1	0,0	0,0	1,0	0,4	58,4	56,1
Fe	1,7	1,2	0,0	1,2	0,1	1,3	0,5	1,5	1,6	3,2	0,9
Mg	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,3	0,0	0,0	0,0
Ca	0,0	0,0	0,0	0,0	0,0	0,0	0,0	40,5	36,8	0,0	0,0
K	0,8	2,2	1,9	1,0	0,5	0,8	0,4	9,9	9,0	0,8	0,6
Na	0,0	47,2	40,6	0,5	0,4	0,5	0,4	2,0	2,6	0,8	0,2
S	0,0	0,0	0,0	0,0	0,0	0,0	0,0	12,5	13,9	0,0	0,0
Cl	0,5	36,1	28,9	1,3	0,5	0,6	0,4	0,0	0,0	0,7	0,2
P	0,1	1,0	0,6	0,5	0,2	0,6	0,2	0,0	0,0	0,4	0,6

Fig. 6: HRSTEM Data of Magnetic Rejects

(particles C & I in Fig.3) and the bigger ones have crystal faces (particle M in Fig.3). Anatase appears as isolated particles (particles A & K in Fig.6; I in Fig.2) and also as adhering to the kaolinite (particles D & E in Fig.2). The smaller the anatase particles, the more they aggregate with kaolinite. The Fe content in anatase ranged between 0.3 to 5.9%. On an average, the 30 analyzed anatase particles contained 2.3 % Fe. In a number of kaolinite particles also, the Ti was estimated. Sometimes the Ti content is high and then the adhering particles are also visible. Most of the 70 analyzed kaolinite particles contain very small percentage of Fe and there were no visible anatase adherences (particle C in Fig. 4). In such cases it is uncertain whether there are several nm – scale Ti particles or the Ti is in the kaolinite lattice. Both options seem conceivable and have similar effects with regard to the degree of whiteness.

Fe Particles

Only few Fe particles, may be as goethite or hematite, have been identified. They are very fine particles of size < 50nm. Particles of this dimension are hard to be detected if they are on or in the kaolinite (particle L in Fig. 4). Only very good dispersion on the film may be able to make them visible. However, the analyses show that at least part of the Fe does exist as independent particles.

Crandallite-Woodhouseite

All samples are found to contain crandallite-woodhouseite minerals which are aluminiferous phosphates / sulphates with Ca, Sr, Ce, La and other ions of similar ionic radius. Some of these particles have been analyzed (particle C in Fig.5). These minerals are generally intense grayish brown in color and bind a considerable part of the trace elements in kaolins.

Other Particles

Apart from the mineral phases, other particles of different compositions have also been detected by the TEM studies as given below.

1. NaCl with a little potassium and gypsum, mainly in the HGMS rejects (particles B & C in Fig. 6)
2. Small needles of gypsum containing Ca, Sand a clearly higher carbon content with a little bit of Fe and Ti in the HGMS rejects (particles H & I in Fig.6)
3. Leaflet shaped unevenly formed particles with Ca, K, Na, S and a clearly higher C content particularly in the flotation rejects which may be residues from the flotation chemicals. The C_{org} content of this sample is high approx.0.44% and total carbon is 0.498% (particles A, B & L in Fig.3)
4. Particles of about 10nm size, some of them containing S and Si are shown in Fig.5 (particle H). Such particles frequently appear in kaolins and are often precipitated organic or humic matter with different inorganic ions like S, Fe, Al or Si. Since the particles are extremely small, their analysis identification is difficult. However, these particles even in small amounts are heavily pigmenting and affect the brightness of kaolin. All samples are found to contain C_{org} in the range 0.05 to 0.084 and total carbon 0.084 to 0.118.

CONCLUSIONS

The XPS study of the Mamuara flotation product clay has ruled out the possibility of any coating of Ti, Fe impurity on the particle surface. The HRTEM combined with microanalysis of selected samples show that most of the Ti is present in the form of individual anatase particles of very small size. A part of the iron forms independent particles (goethite or hematite) of extremely small size. Rest of the iron is bound closer to the kaolinite particles and hence may not be easily separated. They can be either part of kaolinite structure or nano sized independent mineral particles adhering to the kaolinite surface. Regarding the brightness of the samples, the fine grained anatase remaining in the kaolinite has a strong pigment effect because it contains some iron which gives dark color to it. At the same time, this iron content increases the magnetic susceptibility of making the anatase separation a little

easier by HGMS. The dissatisfying degree of brightness in the flotation product can be attributed to these fine grained anatase particles. The influence of iron is difficult to be found out since it is not clear whether the iron is in the kaolinite structure or exists as independent particles. Again, Fe_2O_3 content of 0.4 and 0.25 % in the flotation feed and product samples respectively are relatively low and their influence on the degree of brightness is probably smaller than that of the anatase. The organic matter identified in the samples may be having a pigment effect even at small contents of <0.1% due to their blackish brown color and colloidal distribution. Reductive and oxidative chemical bleaching may reduce the iron and organic carbon content respectively and improve the brightness. The ferriferous smectite identified in the flotation feed (by XRD) is generally greenish yellowish brown color which may also adversely affect the degree of brightness.

ABBREVIATIONS IN TEM

K	: Kaolinite
Ti	: particles rich in Ti (anatase)
Fe	: particles rich in Fe
Cr	: Crandallite-woodhouseite minerals
Sa	: salt, NaCl or flotation chemicals
Gi	: Gypsum
OS	: organic substance
Sm	: smectite

ACKNOWLEDGEMENTS

The authors (SC and PR) are grateful to the Director, RRL for giving permission to publish this work. Thanks are also due to Prof. M.Storr, Univ.of Geigswald, Germany for HRTEM study and Dr.S.Dieckhoff, Fraunhofer Institut fur Fertigungstechnik & Materialforschung, Bremen, Germany for the XPS data. Financial support from Volkswagen Foundation, Hannover, Germany is also gratefully acknowledged.

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