International Journal of Scientific & Engineering Research, ISSN 2229-5518

Reduction of Titanoferrous Impurities from Kaolin by Selective Adsorption of Flocculating Agents

Mahesh M Kulkarni, Gajanan N Jadhav

Abstract: Kaolin clay is used as a filler and pigment in various applications such as paper, paint, rubber, plastics, adhesives, ink and ceramics etc. Major mineral content in crude kaolin clay is kaolinite along with some accessory minerals as quartz, hematite, mica, feldspar, anatase, rutile, illemnite etc. The Fe and Ti bearing minerals play very important role in determining quality of the kaolin, as these minerals impart yellow, pink or darker color to the white kaolin. Conventional beneficiation methods used in kaolin processing are de-gritting, classification and sodium dithionite bleaching, which improves the optical properties of kaolin, wherein reduction of color imparting constituents such as Fe_2O_3 and TiO_2 is marginal. In the present study, these coloring impurities are separated using selective adsorption of water-soluble polymers. Degritted kaolin samples after passing through 45 micron sieve is used in the study for selective flocculation by polyacrylamide based polymers. The effect of pH, zeta potential, and polymer dose on the reduction of impurities is studied. Analytical tools such as XRF, XRD, and STEM techniques are utilized and results are discussed in detail.

Index Terms: kaolin, selective flocculation, polyacrylamide, iron, titania, zeta potential, selective adsorption, brightness

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1 INTRODUCTION

Kaolinite is a mineral belongs to group of aluminosilicates. Kaolin is also known as a “China clay”, as it was discovered at Kauling in China. It is a 1:1 layered silicate belongs to Kaolin group of clay minerals. Structurally, alumina octahedral sheets and silica tetrahedral sheets stacked alternatively forming 1:1 layers. It has a versatile mineral used in diversified industrial applications. Paper, paint, ceramic, and rubber are the major industries, which consumes kaolin for industrial uses [1]. Kaolin is white, soft, inert, non-abrasive, low thermal conductive, plastic clay containing fine grained platelets with high aspect ratio. Kaolin is always associated with other accessory minerals such as quartz, hematite, anatase, feldspar, and mica. These accessory minerals present in kaolin impart color to the kaolin by reducing its commercial value.

Group of scientists have worked on removal of titanoferrous impurities using various techniques. [13] Raghavan et al, studied the effect of high shear pretreatment on removal of TiO_2 by flotation. The TiO_2 of the feed kaolin was 1.06 % and optimized flotation product was of 0.35 %. Research work shows that High shear pretreatment helps in liberation of TiO_2 from kaolin. Influence of pH, rpm, and dispersant dosage were also studied during pretreatment. The froth flotation followed by chemical reductive bleaching is also carried out to evaluate the enhancement in the optical parameters such as brightness. In another study conducted by same group of people shows that SC-HGMS is effective in removing the titanoferrous impurities. The SC-HGMS study was conducted on southern kaolin and western kaolin deposits. Hosseini et al [6] explored the possibilities of bacterial leaching to remove high iron content present in kaolin. Different strains were used to leach iron from kaolin. The feed kaolin clay is highly contaminated with iron of 11% and 42% iron reduction is observed. Chandrasekhar S and Ramaswamy S [3, 14] carried out detailed characterization of impurities by chemical, mineralogical and EPRS studies from both Gujarat and Kerala kaolin. The Kerala kaolin found to be more of ferruginous impurities and Gujarat kaolin found to be more of titanoferrous impurities. Beneficiation studies carried out on High Gradient Magnetic Separation and Citrate-Dithionite-Bicarbonate (CDB) treatments. The free iron from Kerala kaolin is removed by CDB treatment whereas in Gujarat kaolin both free and structural iron associated with titanoferrous impurity was difficult to remove. The crude kaolin contained 1.63 and 0.66 % TiO_2 in Kerala and Gujarat kaolin respectively. Reduction of TiO_2 in case of Gujarat kaolin was from 1.63 to 0.99%. In another study, chemical leaching of kaolin and its effect on thermally treated products was explored.

Felhi et al [4] carried out research work on feasibility studies of kaolin using sodium dithionite bleaching. The mineralogical study of bottom portion of the worked section is found to be of more illitic with higher TiO_2 content. The weak crystalline samples were made suitable for ceramic applications by

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- *Mahesh M Kulkarni is currently pursuing doctor of philosophy program in department of earth sciences, Indian Institute of Technology Bombay, Mumbai, India, PH: 919833213337. E-mail: kulkarnimahesh.in@gmail.com*
- *Gajanan N Jadhav is currently Professor in department of earth sciences, Indian Institute of Technology Bombay, Mumbai, India, E-mail: Jadhav@iitb.ac.in*

reductive bleaching. Ambikadevi V R and Lalithambika M [1] studied the effect of organic acids such as oxalic acid, tartaric acid, ascorbic acid etc, on removal of iron and titania impurities and compared against the magnetic separation studies. Nearly 17% increase in brightness observed in magnetic separation studies. The acid leaching at various temperature is studied and oxalic acid results in best leaching effect at 100 ^{0}C. Andreola et al [2] studied rheological behavior of kaolin in presence of SHMP. Electro kinetic measurement confirmed the SHMP adsorbs on to the surface of kaolin in the study. Rheological behavior affected because of presence of Calcium cations present in clay. Paul et al [11] characterized the TiO_2 impurities present in the Georgia kaolins. Murray et al [10] discussed in detail about effect of mineralogy, chemical composition, viscosity, particle size, shape, brightness, gloss, and opacity of kaolin on paper coating application. Process and engineering aspects of producing engineered kaolin with narrow particle size distribution are also discussed. Yee-Ho and Somsundaram [16] studied the carrier flotation of kaolin, where Calcium ions are used as carriers. Saikia et al [15] studied beneficiation of ferruginous kaolin from Deopani, Assam. Magnetic separation followed by dithionite bleaching is reviewed to enhance the optical properties. Suitability of beneficiated products analyzed for ceramic applications. Asmatulu [12] compared both froth flotation and selective flocculation to remove TiO_2 impurities from Georgia kaolin followed by dewatering studies. Luz A B and Meddea and Larryod et al [8, 9, 5] worked on purification of kaolin by selective flocculation. The flocculants with different anionicity were studied. The high and medium anionicity flocculants performed better in purification. The TiO_2 recovery in flocculated mass is of 80%. In these both studies, the use of Hydroxamate collector resulted in better selectivity of the TiO_2 impurities.

In consideration of economic challenges in reducing the chemical consumption in separation processes of kaolin, in the present studies separation of titanoferrous impurities is studied by collectorless selective flocculation by using modern polymer flocculants. The efficiency of separation is evaluated at different ionic concentration i. e. at two different pH and polymer concentration.

2. MATERIALS AND METHODS

Chemical analysis is carried out using ED X-ray Fluorescence, Shimadzu model EDX-700. Powder XRD was carried out on un-oriented sample with Shimadzu model XRD-6000 operating at 40 kV and 30 mA current using Ni-filtered Cu Kα radiation at a scanning speed of 0.5 2ϑ/min. Quantitative mineralogical analysis is carried out according reitveld curve fitting method using sirquant, CSIRO, Australia software. Scanning electron microscope model no 6500LV, Jeol is used for morphological studies. The Jeol TEM 2100F is used for transmission electron microscope studies. The zeta potential measurements are carried out using Malvern's zetasizer. Optical properties were measured using Hunter lab's colorflex. The commercial available Anionic polyacrylamide based polymers with varying molecular weight are selected for the study. The effect of three different polymers LM-143, MM-149 and MM-349 are evaluated on separation of titanoferrous impurities. Polymer solutions of 0.1 % concentration are prepared using distilled water. Crude kaolin is refined to remove the grit content present by blunging followed by screening on 45 micron sieve and degritted kaolin is used for further studies. The ten percent solid content clay slurry is prepared using distilled water to avoid the ionic influences during polymer adsorption. pH adjusted using ten percent sodium hydroxide solution. Effect of pH on separation of impurities is evaluated at two different pH i.e. at pH eight (natural pH of crude kaolin), at pH nine and pH ten. Clay slurry is mixed using high shear agitator for 30 minutes. Anionic polymers added with mild agitation and allowed to settle for 30 minutes. Flocculated and suspended mass is separated by siphoning the suspended portion. Both the fractions are analyzed for chemical, mineralogical, morphological and optical properties.

3 RESULTS AND DISCUSSION

Crude kaolin analysis represented in Table 1 infers the presence of quartz and titanoferrous impurities.

The TiO_2 content is nearly four percent, which influences the optical property with lesser brightness of 68.8%. The Figure 1 represents the clay behavior at different pH, showing surface charge distribution at various pH. The zeta potential at alkaline pH shows maximum negative value (Jianfeng et al 2006) exhibiting typical kaolin behavior.

At alkaline pH better dispersion (Hu et al 2003) and liberation of titanoferrous impurities is expected because of more number of negative surface charges. The degritted clay sample shows marginal improvement in kaolinite content and less influence on the titanoferrous impurities and brightness. Crude clay pH found to be eight.

Table 1. Crude kaolin and degritted kaolin characterization

Chemical Analysis, %		
	Crude clay	Degritted clay
SiO_2	42.96	42.12
Al_2O_3	37.05	37.54
Fe_2O_3	1.4	1.34
TiO_2	4.03	4.08
LOI	13.5	13.92
Quantitative Mineralogy, %		
	Crude Clay	Degritted clay
Kaolinite	84	87
Quartz	12	9
Anatase	3.6	3.6
Optical Properties		
	Crude clay	Degritted clay
L	81.1	82.7
a	0.48	0.54
b	3.18	3.77
Brightness, %	68.8	69.52

The ionic concentration influences the sedimentation behavior [9] and adsorption of polyacrylamide polymers is controlled by hydrogen bonds between amide groups and metallic surface of mineral impurities present in the clay suspension. The selective adsorption of polymer on impurities present in the degritted kaolin is carried out and the titanoferrous impurities are analyzed in flocculated and suspended mass (product). Efficiency of separation is studied by varying the flocculant dose. The reduction in TiO_2 and Fe_2O_3 is at pH eight and nine is represented in Figure 2, Figure 3 and Figure 4, Figure 5 respectively.

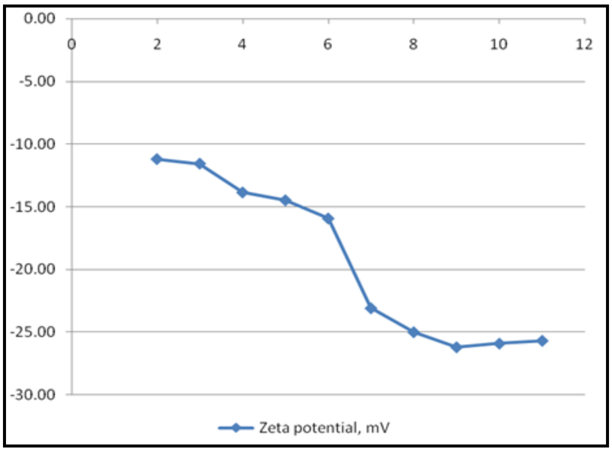

Figure 1. Study of surface charges in degritted kaolin by zeta potential measurement

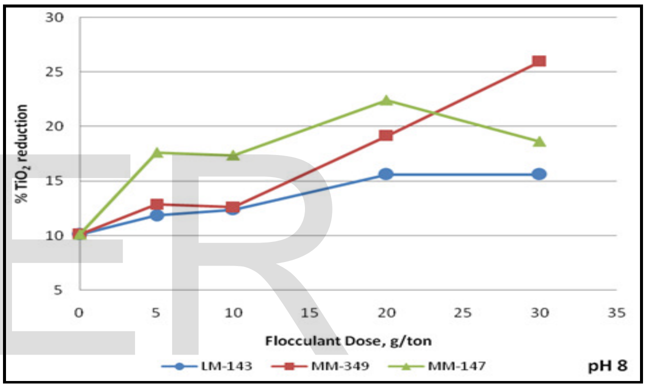

Figure 2. TiO_2 reduction in the product (suspended mass) at pH 8

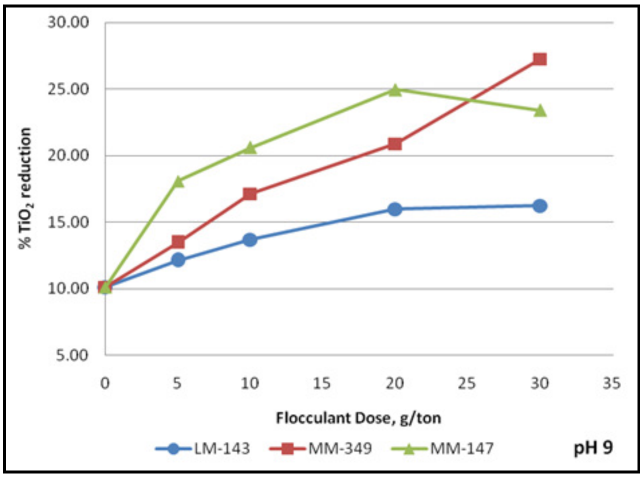

Figure 3. TiO_2 reduction in the product at pH 9

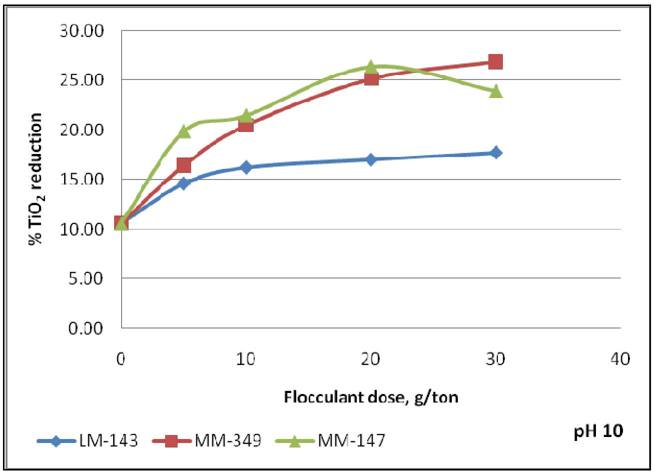

Figure 4. TiO_2 reduction in the product at pH 10

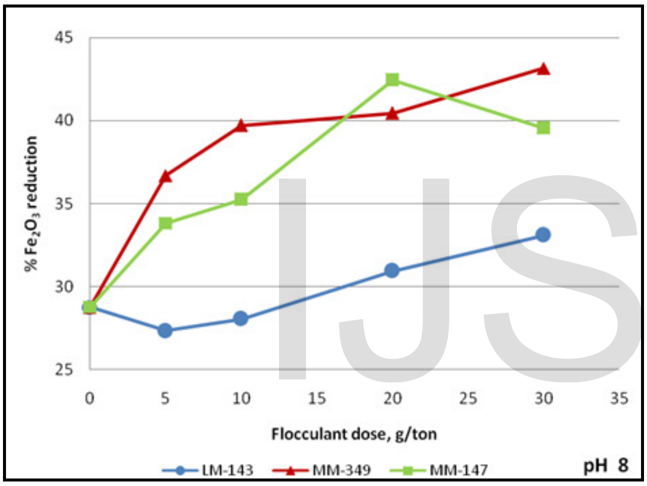

Figure 5. Fe_2O_3 reduction in product at pH 8

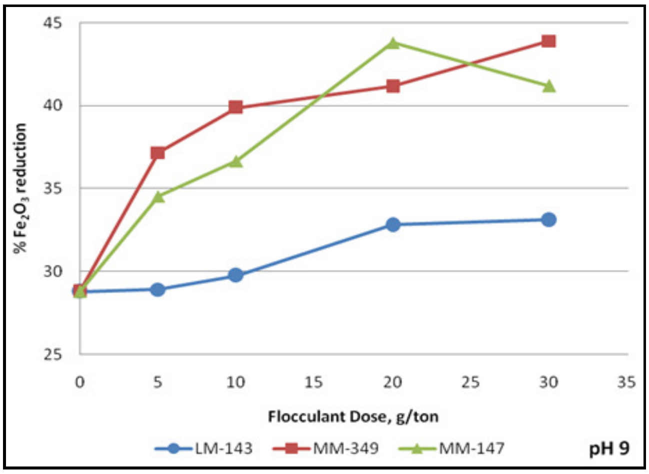

Figure 6. Fe_2O_3 reduction in the product at pH 9

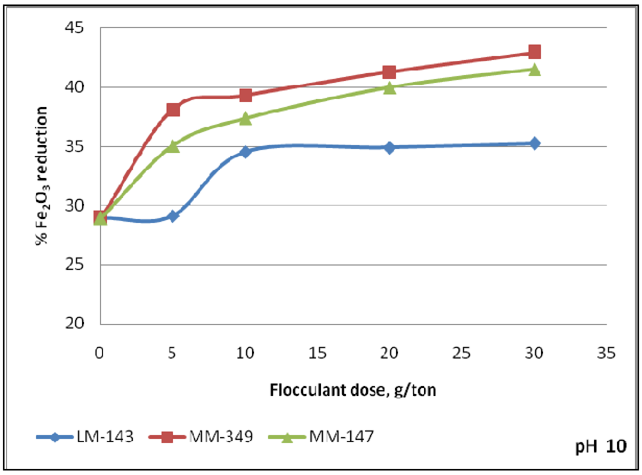

Figure 7. Fe_2O_3 reduction in the product at pH 10

25.94% reduction in TiO_2 is observed using MM-349 flocculant with 30 g/ton dose at pH eight with enhanced brightness of 78.12% and 27.26% reduction in TiO2 with enhanced brightness of 79.51% at pH nine. Similar trend is observed in Fe2O3 reduction by using MM-349 flocculant. At pH, nine the better reduction of impurities and brightness enhancement obtained due to better dispersion of kaolin particles and liberation of impurities, which can be correlated to more number of negative surface charges present at this pH. With MM-147 flocculant, the maximum enhancement in brightness of 80.35% is achieved at 20 g/ton flocculant dose with 24.94% TiO2 reduction at pH nine. MM-147 shows decrease in selectivity of titanoferrous impurities at higher of dose 30 g/ton of flocculant, where the TiO2 reduction dropped from 43.79 to 41.19 % and brightness value fell down from 80.35 to 79.9 % (refer Figure 6 & Figure 7).

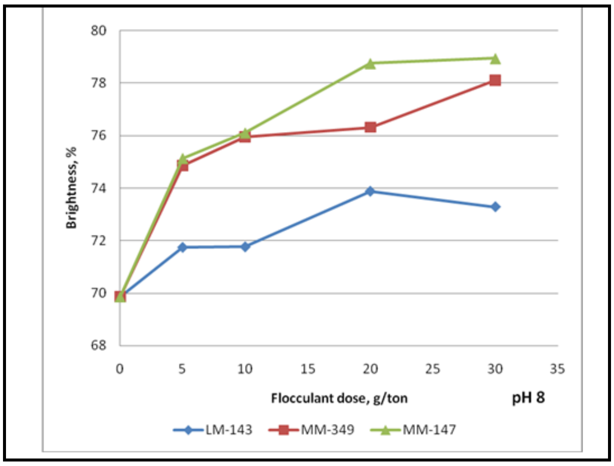

Figure 8. Effect of flocculant dose on enhancement of brightness in the product at pH 8

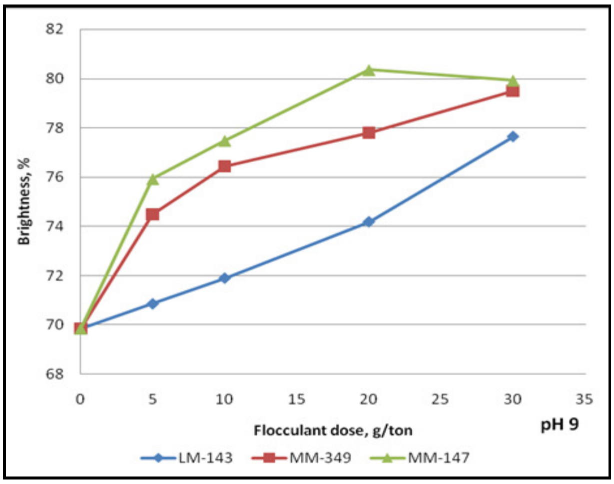

Figure 9. Effect of flocculant dose on enhancement of brightness in the product at pH 9

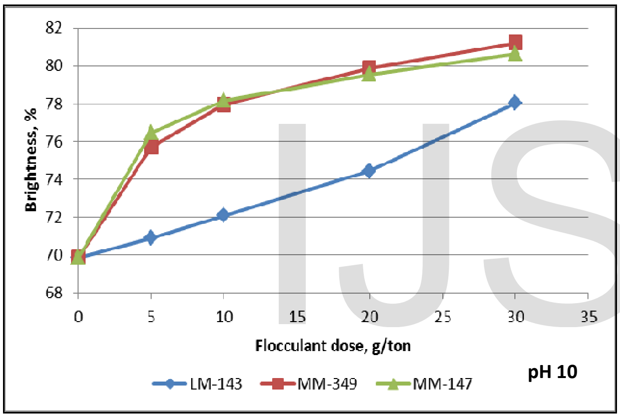

Figure 10. Effect of flocculant dose on enhancement of brightness in the product at pH 10

Performance of LM-143 flocculant in reduction of Fe_2O_3, TiO_2 and brightness enhancement is marginal. Low molecular weight of LM-143 is less effective in adsorbing the metallic surface of titanoferrous impurities. In the present studies all, the grade and recovery data follows the standard patterns as previous works [8, 9]where the maximum grade is achieved with reducing recovery. Figure 8 represents the percentage TiO_2 reduction i.e. grade versus yield curve. The yield of 59% obtained with 42.9% TiO_2 reduction using flocculant MM-349. To understand the adsorption of flocculant on impurities SEM and TEM studies done for fractions generated during the experiment. Flocculant adsorption on titanoferrous impurities is confirmed by STEM analysis and it is represented in Figure 13.

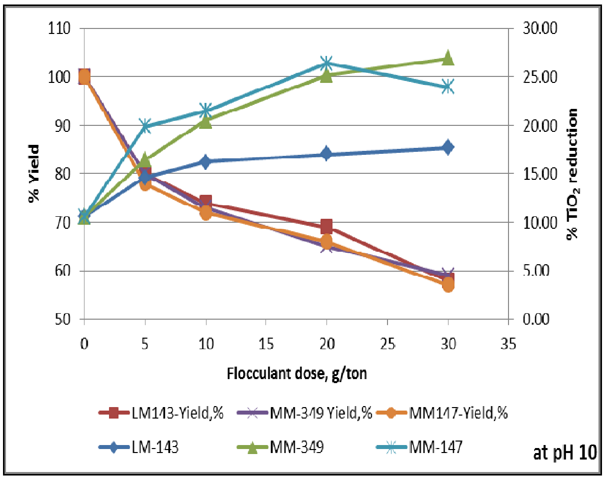

Figure 11. Grade and Yield curves for TiO_2 reduction at pH 10

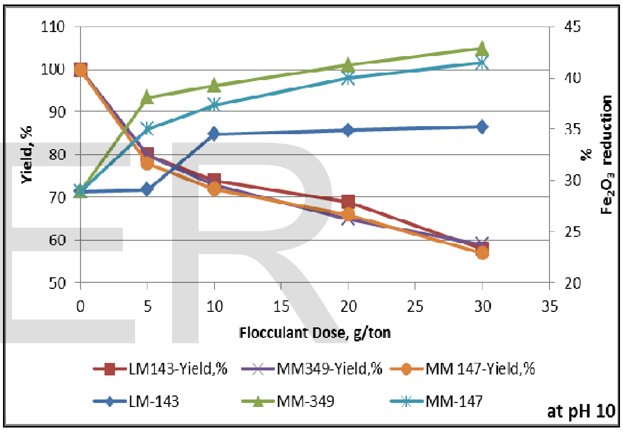

Figure 12. Grade and Yield curves for Fe_2O_3 reduction at pH 10

4 CONCLUSIONS

Crude kaolin characterization shows the presence coloring impurities as TiO2 and Fe2O3. Degritted kaolin shows minimum difference to crude kaolin. The selective flocculation process is efficient in separating impurities from kaolin without using collector. The selective adsorption by flocculants is better effective at pH nine, where negative charges present on the kaolin surfaces help in adsorbing the titanoferrous mineral surfaces by polyacrylamide polymers. Both MM-349 and MM-147 flocculants shows positive results by enhancing the brightness of the kaolin and reducing titanoferrous impurities. MM-147 flocculant resulted in achieving maximum brightness of 80.35% from 69% with minimum dose of 20 g/ton dose. The 60% yield achieved with nearly 25% TiO2 reduction using MM-147. Further scope exists to enhance the brightness by reducing titanoferrous impurities by fine tuning the pH, solid content, effect of dispersing agents, flocculant selection, and selectivity enhancement of impurities by collectors such as hydroxamates and possible alternative methods of separations.

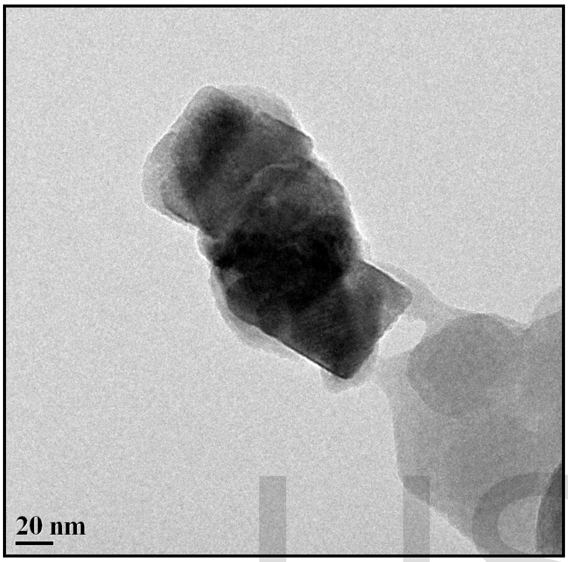

Figure 13. Adsorption of flocculant on to the surface of titanoferrous impurities by TEM analysis

ACKNOWLEDGEMENTS

Authors sincerely thank Mr. Chetan Shah, Chairman, Ashapura Group to providing the constant support and opportunity conduct research work. Authors also appreciate all co-workers, instrument operators for providing help and co-ordination for the research work.

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