

Beneficiation of Libyan Kaolin Ore for Different Industrial Applications

Nagui A. Abdel-Khalek, El-Sayed R. E. Hassan*, Khaled E. Yassin and Khaled A. Selim

Mineral Beneficiation and Agglomeration Department, Mineral Technology Division, Central Metallurgical Research & Development Institute (CMRDI), P.O. Box 87 Helwan, 11722 Cairo, Egypt.

ARTICLE INFO

Article history:

Received: 21 October 2019;

Received in revised form:

10 November 2019;

Accepted: 20 November 2019;

Keywords

Kaolin,
Upgrading,
Magnetic separation,
Bleaching.

ABSTRACT

Kaolin is a clay material consisting of substantially pure kaolinite. Kaolin is used in many industrial applications such as ceramic, paint and paper industries. This paper aims to study, for the first time, the beneficiation of Libya kaolin ore. Attrition scrubbing and classification were used to separate the free silica. Wet high intensity magnetic separation was applied to remove colored contaminants. The kaolinite mineral content increased from 63.5 % to 85 %. The whiteness and brightness of kaolin concentrates were efficiently improved. A final kaolin products containing 0.79 – 0.85% Fe_2O_3 and 0.66 – 0.68% TiO_2 were obtained with whiteness about 85%.

© 2019 Elixir All rights reserved.

1. Introduction

Kaolin is significant industrial clay which is properly contains a hydrated aluminum silicate mineral named kaolinite [1,2,3]. Other kaolin minerals include dickite, nacrite, and halloysite. Pure forms of these minerals are not as widespread as kaolinite, and are usually found together with kaolinite in hydrothermal deposits [2]. Kaolin is also formed in residual or sedimentary modes. In the hydrothermal deposits, the mineral is created due to in-situ weathering or hydrothermal alteration of alumino-silicate parent rocks such as granite. While, in the residual or sedimentary deposits, kaolinite is produced by the deposition of kaolinite formed elsewhere [3,4]. Pure kaolinite has the composition, expressed as oxides, 46.54 % SiO_2 , 39.50 % Al_2O_3 and 13.96 % H_2O . Unique mineralogy and morphology as well as physical and chemical specifications of kaolin make it a versatile raw material appropriate for different applications [3,5].

Actually, kaolin was first used in ceramics and this is perhaps still the best known application. The most important properties for this use are plasticity, strength, and fired color. The particle size of $\sim 2\mu\text{m}$ in the ceramic kaolin is between 55 and 65% while the Fe_2O_3 content is less than 0.5% [6]. The existence of iron oxides in kaolin adversely affects the clay color, and reduces its brightness and refractoriness. This cause a dramatic decrease in its commercial price even a small amount of oxides, hydroxides and hydrated oxides of ferric iron is enough to impart a red to yellow pigmentation to clay deposits [7]. Developed beneficiation flowsheets are well established, particularly in Georgia, USA and Cornwall, UK, to reach the required specification for good quality kaolin concentrates [6]. The Egyptian kaolin for example is hard and massive. It is also low grade so, that it needs beneficiation to be suitable for different industries. Its most industrial applications should have very fine size distribution (90% by weight below $2\mu\text{m}$) and should be of high quality [8]. The primary step in kaolin processing is to separate the abrasive minerals like quartz and undesirable mineral such as mica. This is a simply process in case of a secondary deposit,

but in contrast with the primary deposit as it is more difficult due to the presence of high proportion of the abrasive minerals that have survived the alteration process [9]. It was also determined that high magnetic separators were effective for the nanosize- discoloring elements to produce high brightness clay. Therefore, other processes i.e, flotation and/or selective flocculation can be incorporated to increase the brightness of kaolin clay [10,11]. The iron removal processes can be categorized as physical, chemical, or a combination of both, physical approaches include high intensity magnetic separation, which able to remove iron and titanium impurities, and hydro-cyclones [12, 13, 14].

This work aims at studying the beneficiation of a Libyan kaolin ore. Attrition scrubbing and classification is applied to remove the associated free silica impurities. Wet high intensity magnetic separation is applied to reduce the content of iron oxide and titanium oxide. A central composite design is used to optimize the different variables affecting the process. Acid bleaching is performed in order to efficiently reduce the colored contaminants and to improve the whiteness and brightness of kaolinite.

2. Experimental Methods

2.1. Preparation of kaolin sample

The kaolin sample represents a kaolin ore from a kaolin mines in south Libya. The kaolin sample was crushed, using a Jaw crusher, followed by Roll Crusher, down to 100 % below 16 mm size. This was followed by thoroughly mixing of the whole sample to be homogenous, and then, sampled into representative samples. One of these samples was subjected to evaluation and analysis. The rest of samples were subjected to beneficiation experiments to upgrade their quality.

2.2. Evaluation of kaolin sample

X-Ray Diffraction Analysis (XRD) was carried out using A Philips PW 1730 powder X-ray diffractometer with Fe-filtered Co (K-alpha) run at 30 kV and 20 mA. Routine chemical analysis of samples was conducted using standard method, iron oxide was determined using Atomic Absorption instrument, Analyst 200.

TiO₂ was determined by using spectroscopic technique. L.O.I. (Loss of Ignition) and SiO₂ were determined gravimetrically, complete chemical analysis of samples was conformed using "Philips" X-ray fluorescence (XRF) instrument.

2.3. Sizing and classification of kaolin sample

A crushed sample was subjected to screen analysis using a sieve shaker and a set of screens for 15 min, after which, each fraction on the screens was weight and chemically analyzed.

2.4. Attrition scrubbing and classification processes

The crushed kaolin samples (of – 16 mm) was subjected to attrition scrubbing (De-gritting) process using "Denver" attrition scrubbing machine, to disintegrate the kaolin particles from its associated gangue particles like silica. The experiments were performed for 1 hour at high percentage solids (at solid-water ratio of 60 % solids by weight). The attrited product was classified through screening the produced slurry on screen shaker unit using a 0.075mm screen. Further classification of the produced slurry was performed using hydrocyclone unit to separate the free silica particles of size greater than 0.045 mm. The experiments were performed at the following operating conditions: pressure 18 psi and solid-liquid ratio of 14% solids by weight. The different fractions (+0.074mm, -0.074+0.045mm, and - 0.045mm) were dried, weighted and chemically analyzed.

2.5. Magnetic separation of kaolin sample:

The experiments of magnetic separation of -11 micron kaolin samples were conducted using "Boxmag Rapid" LHW magnetic separator. The separating box (canister) was packed with stainless steel wool. The feed was conditioned to avoid the presence of agglomerate particles. The slurry was fed from bottom to top (anti-gravity) and the magnetic fraction was retained on the stainless steel wool where the non-magnetic kaolinite fraction is collected at the top. The magnetic fraction was taken out of the separating grid by washing with water in the absence of the magnetic field. The field intensity and feed pulp density (solid to liquid ratio) were studied. Magnetic and non magnetic fractions were weighed dried and chemically analyzed [9].

2.6. Acid bleaching of non-magnetic pre-concentrates

The acid bleaching experiments were carried out in a Perspex reactor at the different conditions of temperature, time and bleaching agents at solid-liquid ratio of 25% solid by weight. Two bleaching agents were tested, oxalic acid and Dithionous acid, at a dosage range from 1 to 7 kg/t. At the end of the test, the slurry was filtered and dried in a dryer at 40 °C. Then, the degrees of whiteness and brightness were measured using a computerized whiteness tester.

3. Results and Discussion

3.1. Evaluation of the kaolin sample

3.1.1. X-ray diffraction analysis (XRD)

Figure 1 shows the XRD patterns of the kaolin ore sample. The XRD analysis of the kaolin sample indicated that kaolinite mineral (Al₂Si₂O₅(OH)₄) and illite [(K,H₃O)Al₂(Si₃Al)O₁₀(OH)₂.H₂O] are the main clay minerals. Quartz as silica (SiO₂) represents the main gangue impurities. Anatase (TiO₂) represents minor impurities.

3.1.2. X-ray fluorescence analysis (XRF)

The chemical analysis of the kaolin ore sample showed that, the sample represents low quality grade kaolin where it has low Al₂O₃ content of 24.31 % with high silica content of 62.07 %. The sample has 1.38 % TiO₂ and iron oxide of 1.72 %, Table1.

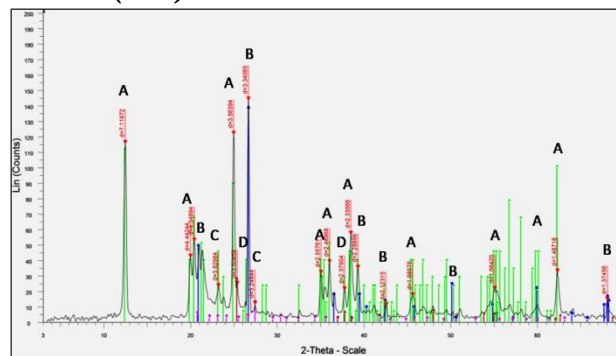


Figure 1. XRD patterns of kaolin sample where A)represents kaolinite, B)represents silica, C) represents illite and D)represents anatase.

Calculation of kaolinite mineral, based on Al₂O₃ content (24.31 %), suggested that the sample contains lower contents of kaolinite mineral (~ 63.5 %) due to the presence of high amounts of free silica. As the alumina/silica ratio in pure kaolinite mineral is 1.18, while this ratio is increased to 2.55 in the studied kaolin sample.

Table 1. Chemical analysis of the kaolin ore sample

Components	Al ₂ O ₃	SiO ₂	TiO ₂	Fe ₂ O ₃	L.O.I.
%	24.31	62.07	1.38	1.72	8.98

Based on the evaluation results of the kaolin ore sample, it has been decided to conduct the following processes:-

a-Attrition scrubbing and classification processes to disintegrate and separate kaolinite from the associated gangue impurities such as free silica.

b-Magnetic separation to reduce the iron bearing minerals (Fe₂O₃ %).

c-Leaching process to improve the degrees of whiteness and brightness through reducing the coloring impurities (Fe₂O₃ % and TiO₂ %).

3.2. Attrition scrubbing and classification processes of kaolin sample

The crushed kaolin sample was subjected to attrition scrubbing process to disintegrate the kaolin particles from the associated gangue particles. The experiments have been performed for 1 hour at high percentage solids (60 % solids by weight).The attrited product was classified through screening and then a hydrocyclone unit to separate free silica particles of size greater than 0.045 mm.

Table 2 shows the chemical analysis of the produced kaolin fractions after attrition scrubbing and classification processes. These results indicated that the coarse fraction (+0.075 mm) is heavily contaminated with silica (60.66%) and iron oxide (5.22 %) contents. Also, the medium fraction (-0.075+0.045mm) is heavily contaminated with silica (80.5 %). Therefore, both fractions were rejected as final tails.

On the other hand, the quality of the fine fraction (- 0.045mm), which is considered as kaolin pre-concentrate, is significantly improved in comparison to the run-of-mine (ROM) kaolin sample, Table 2. The content of silica is reduced from 62.07 % in the ROM sample to 56.11 %, and consequently L.O.I. content is increased from 8.98 in ROM to 10.28 % in such pre-concentrate product. Also, the iron oxide content is decreased from 1.72 % to 1.52 %.

This means that the kaolinite mineral is increased from about 63.5 % in ROM to about 73.4 % in the finest kaolin fraction (-0.045mm), i.e., the attrition scrubbing and classification processes helped in increasing the kaolinite mineral by about 10 units.

Table 2. Results of attrition scrubbing and classification of kaolin sample.

%	Produced Kaolin Fractions			ROM
	+ 0.075 mm	-0.075 + 0.045 mm	-0.045 mm	
Wt %	7.50	15.0	77.50	100
L.O.I.	3.33	3.96	10.28	8.98
SiO ₂ %	60.66	80.50	56.11	62.07
Fe ₂ O ₃	5.22	1.60	1.52	1.72

In order to improve the separation of fine silica impurities from the kaolin pre-concentrate (of -0.045mm), a sample was subjected to further classification using a "cyclosizer" unit. This unit is able to separate particles down to about 11 micron (0.011mm). The results are shown in table 3.

The results showed that the size fractions from +44 to +11 micron have very small L.O.I. %, and in turn, their content of kaolinite is minimum. For this reason, these size fractions should also be rejected, because they are heavily contaminated with free silica.

Table 3. Results of separation using Cyclosizer unit

Size, micron	Wt., %	L.O.I., %
+44	0.62	1.39
+35	0.79	2.23
+25	1.40	2.99
+15	2.95	4.27
+11	3.80	5.15
-11	90.44	11.89

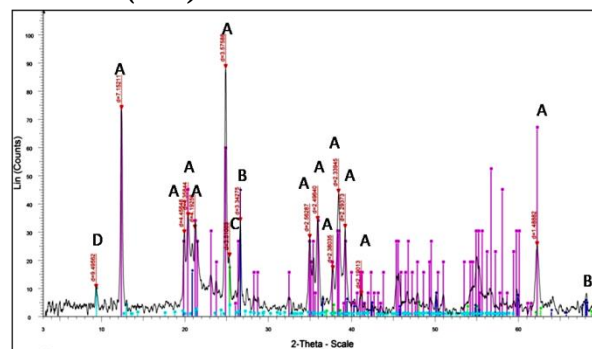
On the other hand, the results indicate clearly that percent of L.O.I. is increased in the finest kaolin product, -11 micron, to about 11.9 %. This means that the content of kaolinite mineral in such fine kaolin product is about 85 % kaolinite.

Table 4 shows the chemical analysis of the final product of -11 micron in size. The results indicated that the quality of such kaolin product is significantly improved in comparison to the ROM sample where the kaolinite mineral is significantly increased from about 63.5 % in ROM sample to about 85.0 % in such finest kaolin concentrate product. This is due to the reduction of total silica from 62.07 % to 56.5 % and, in turn, the L.O.I. % increased from about 8.98 % to 11.9 %. At the same time, the Fe₂O₃ and TiO₂ contents decreased from 1.72% and 1.38% to 1.25% and 1.05% respectively. The XRD pattern of -11 kaolin fractions confirms the increase of kaolinite mineral and decrease of free silica compared to ROM sample, Figure 2. It should be mentioned, that this product could be used in sanitary ware and ceramic manufacture.

Such kaolin pre-concentrate product could be subjected to magnetic separation process in order to reduce the content of iron oxide.

Table 4. Chemical analysis of the fine product of size below 11 micron

%	Kaolin product (-11 micron)	ROM kaolin
SiO ₂	56.54	62.07
Fe ₂ O ₃	1.25	1.72
TiO ₂	1.05	1.38
L.O.I.	11.89	8.98
Kaolinite	85	63.5

**Figure 2. XRD patterns of kaolin concentrate where A)represents kaolinite, B)represents silica, C) represents anatase and D)represents illite.**

3.3. Application of Magnetic Separation Process on Kaolin Pre-concentrate

In order to improve the grade of kaolin pre-concentrate (-11 micron in size), it was subjected to magnetic separation using a Box Mag wet high intensity magnetic separator. The separation process was performed at different conditions of field intensity and feed pulp density. An experimental design technique, Central Composite Design, is utilized for the optimization of magnetic separation process. This study permits the investigation of the effect of field intensity and feed pulp density on the magnetic separation.

The best parameters were estimated according to the design using a second order polynomial function. Using this function a correlation between studied parameters and response was created. The general form of this equation is: [14]

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2$$

where Y is the predicted response; Fe₂O₃ and TiO₂%, X₁ and X₂ are studied variables field intensity and feed pulp density; β_{ij} are equation constants and coefficients.

The analysis of variance, ANOVA, was utilized in order to evaluate the statistical parameters. The analysis of variance data for the magnetic separation system ensures the well convenience of the experimental results to the polynomial model equation and therefore the accuracy of this model, Table 5. The model F-values of 592 and 309 indicates the model is significant. The Adequate Precision ratios of 68.8 and 49.7 imply an adequate signal.

Figure 3a, b shows the response surface for the kaolin magnetic separation at different values of the studied factors. It is shown that a high field intensity value is required for obtaining efficient separation of the magnetic impurities, Fe₂O₃ and TiO₂, from the non magnetic kaolin product. Therefore, increasing the field intensity to a maximum value, 0.9 tesla, caused a considerable removal of both Fe₂O₃ and TiO₂ from kaolinite. Moderate values of feed pulp density are recommended for efficient magnetic separation process. Increasing feed pulp density more than 14% resulted in bad distribution of the magnetic and nonmagnetic particles and caused crowding of particles inside the stainless steel canister and therefore reduced the separation efficiency.

The best optimum parameters of the central composite design of "boxmag rapid LHW" magnetic separator are: 13% feed pulp density and maximum field intensity (0.9 tesla), Figure 4. Applying these optimum parameters, the contents of Fe₂O₃ and TiO₂ were reduced from 1.25% and 1.05% to 0.99% and 0.82% respectively.

Table 6 shows that there is a considerable reduction in the coloring bearing minerals. The iron oxide (Fe₂O₃%) in non-magnetic kaolin products was successively reduced from

1.25 % to about 0.99 %. Interestingly, such reduction in the contents of coloring impurities reflected positively in improving the degrees of whiteness and brightness of the non-magnetic kaolin products which have been raised up to 61.82 and 84.41 % respectively.

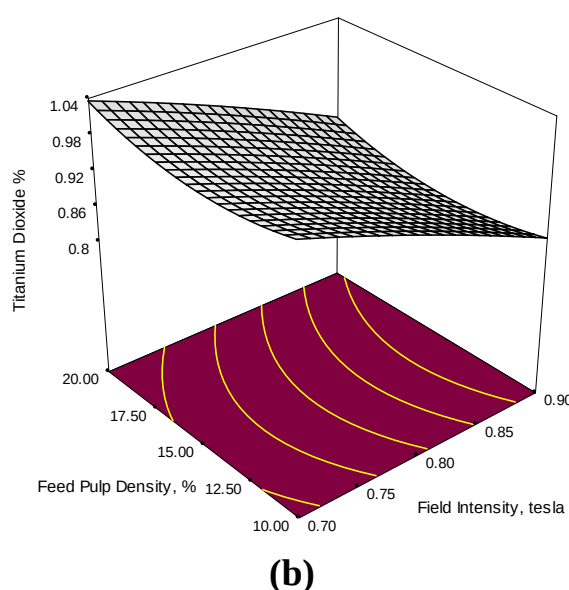
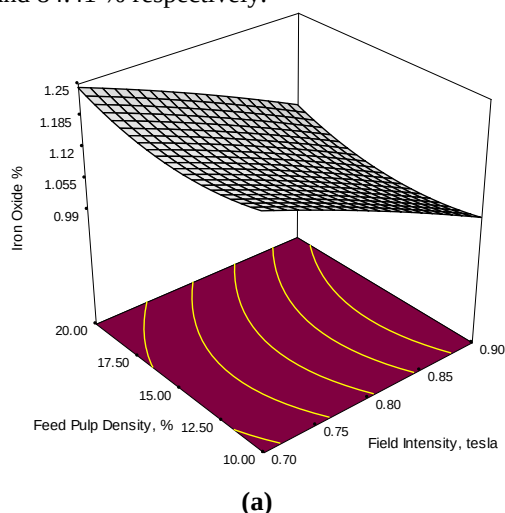


Figure 3. The response surface plots of removal of (a) iron oxide and (b) titanium dioxide from the main effects of boxmag magnetic separator variables.

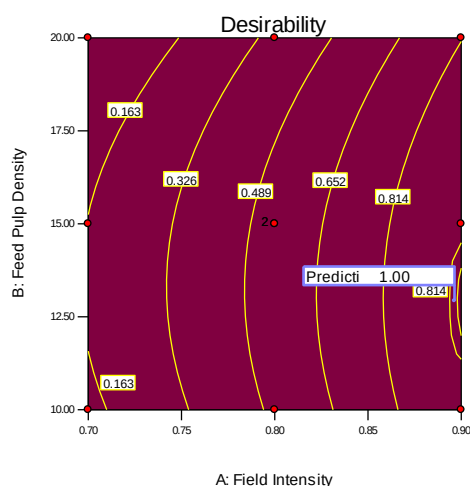


Figure 4. Optimization of the separation process using "Boxmag rapid LHW" magnetic separate

Table 5. ANOVA for response surface for kaolin magnetic separation

The statistical parameters	Magnetic Separation of Kaolin	
	Fe ₂ O ₃ %	TiO ₂ %
The standard deviation	0.0004	0.0005
R-Squared	0.998	0.997
Adequate Precision	68.8	49.7
The model F-values	592	309

Table 6. Results of magnetic separation of kaolin pre-concentrate (-11micron in size).

%	Magnetic impurities	Non Magnetic product
Weight	8.20	91.80
SiO ₂	49.29	57.22
Fe ₂ O ₃	4.62	0.99
TiO ₂	3.45	0.82
L.O.I	11.94	12.79
Whiteness	43.18	61.82
Brightness	57.65	84.41

3.4. Acid Bleaching of Non-Magnetic Kaolin Products

The non-magnetic kaolin concentrate was subjected to a bleaching process to improve the degree of whiteness and brightness of the final kaolin concentrates. Different variables were studied in order to optimize the process.

The results in Figures 5-6 showed leaching process for the non-magnetic concentrates can improve the grade of these concentrates. The results showed that there a further reduction in the iron oxide content. An efficient decrease in Fe₂O₃ and TiO₂ was obtained at temperature of 90 °C during 1 hour. Increasing the dose of oxalic acid up to 5.0 kg/t helped in decreasing the content of Fe₂O₃ and TiO₂ from 0.99% and 0.82% to 0.79% and 0.68% respectively. On the other hand, addition of 5.0 kg/t of dithionous acid decreased the content of Fe₂O₃ and TiO₂ from 0.99% and 0.82% to 0.85% and 0.66% respectively, at the same time increased the degrees of brightness (64.11 %) and whiteness (85.41%), Table 7.

Table 7. Comparison between oxalic acid and dithionous acid as bleaching agents

Bleaching agent	Dose, kg/ton	Fe ₂ O ₃ %	TiO ₂ %	Brightness %	Whiteness %
Oxalic acid	5.00	0.79	0.68	62.50	84.50
Dithionous acid	5.00	0.85	0.66	64.11	85.41

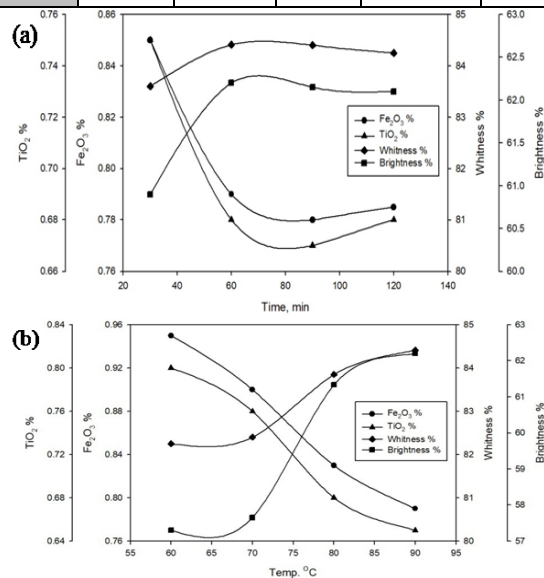


Fig 5. Study the effect of a) time and b) temperature on the bleaching process.

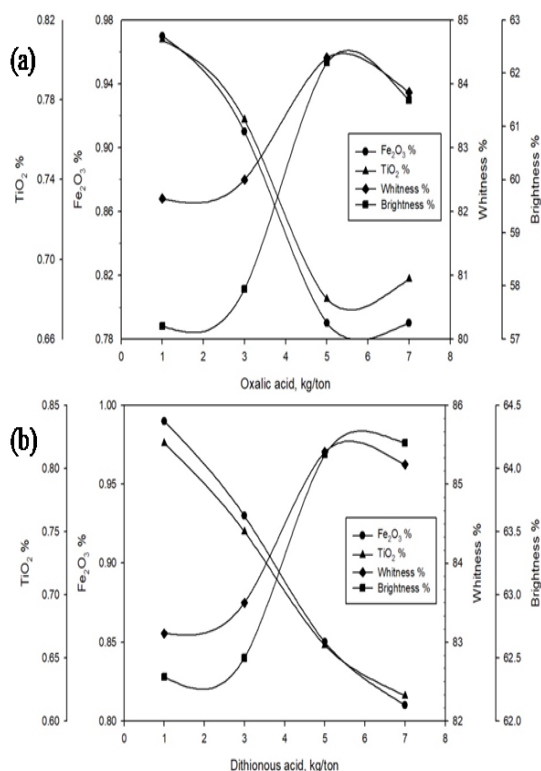


Fig6. Study the effect of a) oxalic acid and b) dithionous acid as bleaching agents.

Conclusions

This paper aimed to study, for the first time the upgrading of a Libyan kaolin ore to be suitable for various industrial applications. The chemical analysis of the kaolin sample showed that the sample contains low content of kaolinite mineral (~63.5 %) and in turn high amount of free silica as impurities. The kaolin sample contains, also, iron oxide of 1.72 % and about 1.38 % TiO₂. The attrition scrubbing followed by multi-classification using screen and hydrocyclone helped in de-gritting the kaolin slurry and removal large amount of free silica. Therefore, the content of kaolinite mineral increased from about 63.5 % to 85 %. Applying magnetic separation process for kaolin slurry helped in considerable reduction of Fe₂O₃ and TiO₂ contents from 1.72% and 1.38% to 1.25% and 1.05% respectively. Applying leaching process for the non-magnetic kaolin concentrate reduced Fe₂O₃ and TiO₂ contents down to 0.79% and 0.68% respectively. Such reduction in the contents of coloring impurities reflected positively in improving the degrees of whiteness and brightness of bleached products which increased up to 84-85 % and 63-64 % respectively. Both kaolin products from magnetic separation and leaching satisfy processes the requirements for sanitary ware, ceramic, and porcelain, as well as filler materials.

Acknowledgment

The authors would like to acknowledge: M. M. Abdallah and A. H. El-Menshaw, PhD students at Minerals Beneficiation and Agglomeration Department, Minerals Technology Division, Central Metallurgical Research & Development Institute, for their efforts during this work.

References

- [1] L. M. S. De Mesquita, T. Rodrigues and S.S. Gomes "Bleaching of Brazilian kaolins using organic acids and fermented medium". Miner. Eng. Vol.9, pp., 965–971. 1996.
- [2] H. H., Murray "Chapter 2 structure and composition of the clay minerals and their physical and chemical properties". In: Haydn, H.M. (Ed.), Developments in Clay Science. Elsevier, pp. 7–31. 2006.
- [3] A. Zegeye, S. Yahaya, C. I. Fialips, M. L. White, N. D. Gray and D. A. C Manning, "Refinement of industrial kaolin by microbial removal of iron-bearing impurities" Appl. Sci. vol.86, pp.47–53, 2013.
- [4] A. J. Bloodworth, D. E. Highley, and C. J. Mitchell "Industrial minerals laboratory manual kaolin, mineralogy and petrology series". British Geological Survey, Nottingham. 1993.
- [5] H. W. Ryu, K. S. Cho, Y. K. Chang, S. D. Kim and T. Mori, "Refinement of low-grade clay by microbial removal of sulfur and iron compounds using Thiobacillus ferro oxidans" J. Ferment. Bioeng. Vol. 80, pp.46– 52. 1995.
- [6] N. A Abdel-Khalek, "The Egyptian kaolin: an outlook in the view of the new climate of investment" Applied Clay Science. vol, 15 pp. 325-336. 1999.
- [7] M. R. Guo, Y. M. Lin, X. P. Xu and Z. L.Chen, "Bioleaching of iron from kaolin using Fe (III)-reducing bacteria with various carbon nitrogen sources". Appl. Clay Sci. vol.48, pp.379–383. 2010.
- [8] N. A. Abdel-Khalek, K. A. Selim, S. E. Mohammed, H. H. El-Hendawy and R. M. Elbaz, "Interaction between Kaolinite and Staphylococcus Gallinarum Bacteria" Journal of Mining World Express, Vol. 3, 2014.
- [9] M. K. Abd El-rahman, M. A. Youssef, N. H. Helal, M. M. El-Rabiei and S. R. Elsaiedy, "Experimental design technique on recovery of fine cassiterite from Igla placer ore of Egypt" The Journal of Ore Dressing. Vol.,11 pp., 24-32. (2017)
- [10] M. R. Hosseini and A. Ahmadi, "Biological beneficiation of kaolin: A review on iron removal". Applied Clay Science vol.107, pp238–245. 2015.
- [11] D. A Refaei, M. K. Abd El-rahman, I. A, Ibrahim, F. Eldears and A.T. Kandil, "Improvement the Quality of Egyptian Kaolin for Industrial Applications" Int J Adv Tech. nol, pp1-8: 174. 2017.
- [12] F. H. Abdel El-Rahiem, K. A. Selim and N. A. Abdel-Khalek, "Some Parameters Affecting Beneficiation of Fine Kaolin Particles", Journal of Ore Dressing, JOD, V. 11, Issue 22, pp. 1-8, 2009.
- [13] F. H. Abdel El-Rahiem, M. S. Hassan, K. A. Selim and N. A. Abdel-Khalek, "Evaluation and Beneficiation of Syrian Kaolin for Different Industrial Applications", Journal of Ore Dressing, JOD, V. 10, Issue 19, pp. 34-41. 2008
- [14] El-Sayed R. E. Hassan, N. A. Abdel-Khalek, M. A. Youssef, M. M. Abdallah and A. H. El-Menshaw, "Recovery of albite and mica from Egyptian Abu Dabbab ores using gravity and magnetic separation techniques" Australian Journal of Basic and Applied Sciences.11: 115-123. 2017.