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CARRIER FLOTATION OF ULTRAFINE EGYPTIAN KAOLIN

This paper aims to study the amenability of application of the carrier flotation process for removing the anatase impurities, associated with the Egyptian kaolin pre-concentrate (~80 wt. % below 2 μm) to be suitable for paper coating and fine ceramic industry. The tests were carried out using sodium silicate as a depressant and oleic acid as a collector. Limestone was used as a carrier in these tests. The size of the carrier as well as its quantity in the pulp were studied. The results showed that the size of the carrier played a major role in determining the efficiency of the carrier flotation process where a significant improvement in the grade of the concentrate was obtained by decreasing the carrier grain size. The TiO_2% decreased to its minimum content (0.6%), in comparison with 1.52% in the feed sample, with its lowest retention ratio when a carrier of grain size –25 +10 μm was used. At such optimum carrier size the degree of whiteness reached its highest value (90) in comparison with 56 for the feed sample. At the same time, the quantity of the carrier in the flotation pulp had no greater influence on the grade of the product. The results showed also that the carrier flotation process can give a concentrate with TiO_2% similar to that obtained with the conventional froth flotation technique in presence calcium acetate as an activator, yet the carrier flotation technique has the advantage of reducing the long conditioning time needed for the pulp with the reagents in the conventional technique. The flotation mechanism was discussed.

INTRODUCTION

Kaolin finds many industrial applications and new ones are still being discovered. It is a unique industrial mineral because it is chemically inert over a relatively wide pH range, is white, has good covering or hiding power when used as a pigment or as an extender in coated films and filling applications. Many grades of kaolin are specially designed for specific uses, in particular for paper, paint, rubber, plastics and ceramics (Murray, 1963; Industrial Mineral, 1971).

Kaolin is present in Egypt in many localities but it is of low grade. Beneficiation of Egyptian kaolin, by attrition scrubbing and classification by multi-cycloning for application in paper and ceramics proved its technical viability. However, the still higher anatase (TiO_2) content of such produced concentrates hindered their application in fine ceramics or in paper coating (Youssef, 1994).

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The flotation process may be conceptualized in terms of a large number of sub-processes, most of which are still rather poorly understood (Trahar and Warren, 1976; Chander,1978). Because of the extremely complicated physico-chemico-mechanical conditions existing in the flotation process, the problems associated with the presence of fine particles are most pronounced in flotation. There is a general agreement that flotation decreases with a decrease of size in the fine particle range.

The process of slime coating refers to the attachment of fine particles to larger particles. Such slime coating can be detrimental to flotation in several ways. However, fine particle coatings or slime coatings are not always undesirable in flotation and it is the basis of carrier flotation/ultraflotation process (Chia and Somasundaran, 1983). This paper aims to study the amenability of application of the carrier flotation process for removing ultrafine particles of the anatase impurities associated with the Egyptian kaolin pre-concentrate to be suitable for paper coating industry. The main operating parameters affecting the carrier flotation technique were studied.

EXPERIMENTAL

Materials

A representative pre-concentrate kaolin sample of El-Tih locality, Sinai Peninsula, Egypt, was used as a feed for flotation tests. This pre-concentrate sample was prepared according to a flowsheet adopted on pilot scale at CMRDI, Egypt (Youssef, 1994). This flowsheet was based on using the “Denver” attrition scrubber as a blunger for degritting of kaolin. The degritted kaolin ore was screened, the oversize of which (the grit) was evaluated for tile manufacture and the undersize was dumped to a spiral classifier. Separation of intermediate size quartz and feldspar occurs in this step and the classifier underflow product, was either dumped or recycled to the attrition scrubber depending on its quality. The classifier overflow product was then delivered to the 3” hydrocyclone for further classification. The hydrocyclone overflow is taken as a pere-concentrate for this study (Youssef, 1994).

A pure limestone sample was used as a carrier in flotation tests. The size analysis of the kaolin sample was conducted using the pipette method while that of limestone was performed by a “Warman” cyclosizer. Each fraction was dried and weighed.

Laboratory grade oleic acid and technical grade sodium silicate supplied by Adwic Co., Egypt, were used as a collector and a depressant respectively in all flotation tests. Analytical grade sulfuric acid, sodium carbonate and ammonium hydroxide, from BDH chemicals, UK, were used for pH regulation during the flotation experiments.

Methods

All flotation tests were carried out using a "Denver D12" flotation machine with a 1.5 liter stainless steel container. In each flotation test, about 300 g of kaolin was conditioned, unless otherwise mentioned, with the required weight of the carrier at alkaline pH (10.5) adjusted by sodium carbonate in presence of 1 kg/ton of sodium silicate at impeller speed of 2500 r.p.m. The collector (1 kg/ton) was prepared as an ammonium salt of oleic acid by agitating certain amounts of oleic acid and ammonium hydroxide (4:1 wt/wt ratio) in 100 ml water volume for 15 min. This prepared solution was added to the pulp and conditioned for a certain period at a solid/liquid ratio of 30%, and then flotation was carried out at 2000 r.p.m. At the end of the flotation test, both the floated and non floated fractions were treated with acetic acid, diluted with water in a ratio of 1:1 to dissolve the carrier before drying, weighing and analyzing their TiO_2 content. The degree of whiteness was measured by Dr Lange whiteness tester. In these carrier flotation tests the size fraction of limestone below 45 μm, unless otherwise mentioned, was used as a carrier. In determining the role of carrier size the following size fractions are used: –0.21 +0.106, –0.106 +0.074, –0.074 +0.045 and –0.045 mm. Meanwhile, the following sub-sieve size fractions, separated by the cyclosizer, were used: –45 +33, –33 +25, –25 +15 and –15 +11 μm.

Characterization of the samples

Complete chemical analysis of the kaolin pre-concentrate sample showed that it contains higher amounts of Al_2O_3 (36.40%) and SiO_2 (47.58%). This means that the concentration of the kaolinite mineral is high (~94.64%). The kaolin sample contains a relatively high content of TiO_2 (~1.52%). The XRD analysis of the kaolin sample depicted that the kaolin mineral is mainly present as kaolinite and the main associated gangues are quartz and anatase. The sample has 0.73% Fe_2O_3. The loss on ignition (L.O.I.) is 13.58%, which is normal in case of pure kaolinite, Table 1. On the other hand, the size analysis of the kaolin pre-concentrate sample showed the very fine grain size distribution of the sample where about 79.92 wt. % below 1.95 μm.

Table 1. Chemical analysis of the kaolin sample

Constituent	Assay,%	Constituent	Assay,%
Al_2O_3	36.40	MgO	0.146
SiO_2	47.58	Na_2O	0.036
TiO_2	1.52	K_2O	0.22
Fe_2O_3	0.73	Soluble Salts	0.071
CaO	0.11	L.O.I.	13.58

Meanwhile, the chemical analysis of the limestone sample indicated its purity. It contains about 55.85% CaO and 43.76 wt. % loss on ignition (L.O.I.). The different size fractions are also pure as indicated with nearly constant values of CaO (55.15 –55.85%) and L.O.I (43.22–43.83%) which are in a good agreement with the theoretical values (56% and 44% respectively).

Definitions

In evaluating the flotation results, the following definitions are used:

Retention ratio for TiO_2 (R.R.): ratio of % TiO_2 in the cleaned clay product to the calculated % TiO_2 in the feed. The lower the retention ratio, the purer is the kaolin concentrate. This value varies from 1.0 for no separation to zero for complete separation.

Coefficient of separation (C.S.) = (total wt. % of concentrate + total amount TiO_2 rejected (%) – 100)/100. This value varies from zero for no separation to 1 for complete separation.

Amount of TiO_2 removed (%): weight of total TiO_2 rejected into the floated tailing expressed in terms of percentage of the calculated total weight of TiO_2 in the feed (Wang and Somasundaran, 1980).

RESULTS AND DISCUSSION

Effect of amount of the carrier

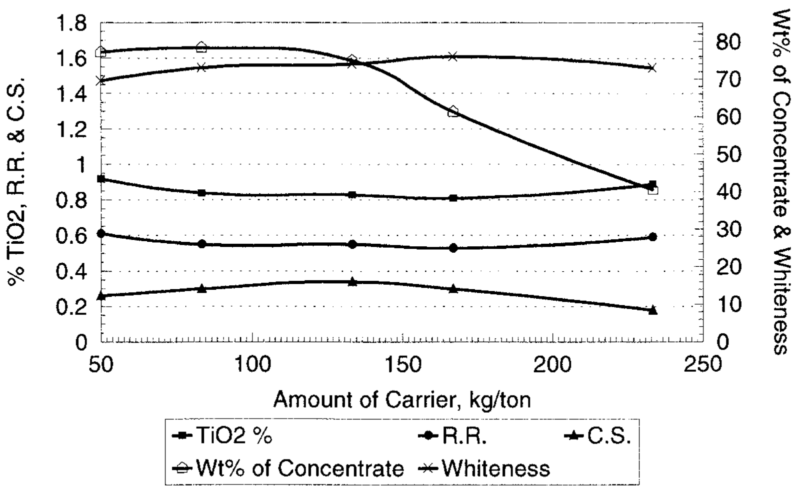

Fig. 1. Effect of amount of carrier on the efficiency of the carrier flotation of kaolin: (carrier size –45 μm, sodium silicate 1kg/ton, oleic acid 1kg/ton, pH 10.5, conditioning time 35 min)

Figure 1 shows the effect of changing the amount of limestone, as a carrier, on the efficiency of the flotation process. In these carrier flotation tests the size fraction of limestone below 45 μm was used as a carrier using 1 kg/ton of each of sodium silicate and oleic acid and at pH 10.5. The conditioning time of the pulp with oleic acid was fixed at 35 min. It is clear that the amount of carrier can determine the selectivity and efficiency of the process. The TiO_2% was reduced from 0.92% at a carrier quantity of 50 kg/ton to 0.80% with increasing the amount of carrier 133.3 kg/ton. Similar results had been mentioned by other authors (Chia and Somasundaran, 1983; Wang and Somasundaran, 1980). However, further addition of the carrier (e.g.~233.3 kg/ton) deteriorated the efficiency and selectivity of the flotation process where the wt. % of concentrate was dramatically reduced from about 78.3% to 40.6%. This was, also, reflected by significant reduction in the whiteness and C.S. as well as with an appreciable increase in the R.R value (Fig. 1).

The improvement in separation of anatase impurities while adding a considerable amount of carrier could be related to the expected increase in the formation of carrier–anatase aggregates, instead of anatase–anatase ones in case of absence of carrier, thereby facilitating their collision with air bubbles and consequently the efficiency of the flotation process will be improved.

Effect of conditioning time of the pulp with oleic acid

Trahar and Warren (1976) have mentioned, based on the flotation rate studies, that ultrafine particles float more slowly than those of intermediate sizes. Moreover, they found that each of the ultrafine size fractions may be further subdivided into slow and fast floating components. The decrease in the rate of flotation of slow component appears to be the main reason for the slow overall flotation rate of the ultrafines. In the mean time, Woodburn et al. (1971) argued that the rate of flotation was equal to the product of three factors: the rate of collision between particles and bubbles, the probability of adhesion, and the probability that the adhering particles would not be detached subsequently. Thus, the flotation rate will depend, among other factors, on the particle size. The lower the particle size the slower the flotation rate. The effect of particle size will, then, be a predominant phenomenon in the flotation of kaolin since the flotation feed contains about 79.92 wt. % below 1.95 μm. This means that the probability of collision between particles and bubbles will be minimum and consequently the flotation process may become a function of time.

Thus, at longer conditioning time the probability of formation of anatase–anatase aggregates may increase which in turn will improve both their collision rate with air bubbles and the probability of adhesion. This was proved experimentally in flotation of the present kaolin sample in absence of carrier where the authors found that the optimum conditioning time was 35 min (Abdel-Khalek et al, 1996). For this reason, a series of carrier flotation tests, in this study, were conducted at varying conditioning time. The tests were performed using about 83.33 kg/ton of the carrier of size fraction below 45 μm. One kg/ton of each of sodium silicate and oleic acid was used as a depressant and a collector respectively while the pH was maintained at 10.5. The results of these flotation tests are shown in Table 2.

Table 2. Effect of conditioning time in presence of carrier

Conditioning time, min	TiO_2 %	% TiO_2 removed	R.R.	C.S.	Whiteness
10	0.909	70.11	0.59	0.26	76.1
20	0.85	77.5	0.56	0.28	78
35	0.83	78.31	0.55	0.28	78

The results in Table 2 indicated that the conditioning time with oleic acid in presence of carrier can be significantly reduced from 35 to 20 min without affecting the selectivity or the efficiency of the process. The TiO_2 content, R.R. and C.S. remained constant upon decreasing the conditioning time to 20 min. However, the TiO_2 content and whiteness were adversely affected by further decrease of the conditioning time to 10 min. It seems from these results that the conditioning time can be decreased to 20 min instead of 35 min without affecting the grade and whiteness of the obtained concentrate. Such significant reduction in the conditioning time will decrease the power consumption needed for the process. The reduction of conditioning time in carrier flotation may be related to the improvement of the aggregation of the anatase–carrier aggregates the grain size of which are significantly larger than that of anatase–anatase ones, in conventional froth flotation. The conditioning time of oleic acid with the former aggregates should be shorter than in the latter case. It is, also, clear from the results that further decrease of conditioning time to 10 min results in a slight increase of TiO_2%, which may be probably due to poor adsorption of oleic acid on the anatase–carrier aggregates.

Effect of the grain size of the carrier on anatase flotation

Figures 2 and 3 show the effect of application of a carrier of different size fractions on the efficiency of the carrier flotation of anatase. Figure 2 shows the usage of the size fractions –0.21 +0.106, –0.106 +0.074, –0.074 +0.045 and –0.045 mm while Figure 3 depicts the results of using the following sub-sieve fractions as carrier: –45 +33, –33 +25 and –25 +10 µm. All flotation tests were performed at pH 10.5 using about 83.33 kg/ton of the carrier. One kg/ton of each of sodium silicate and oleic acid was used as a depressant and a collector, respectively.

The results in Fig. 2 indicated that the TiO_2 content was gradually decreased from 0.98% to 0.84% with decreasing the size of the carrier from –0.21 +0.106 mm to –0.045 mm. At the same time, the C.S., R.R. and whiteness values were improved.

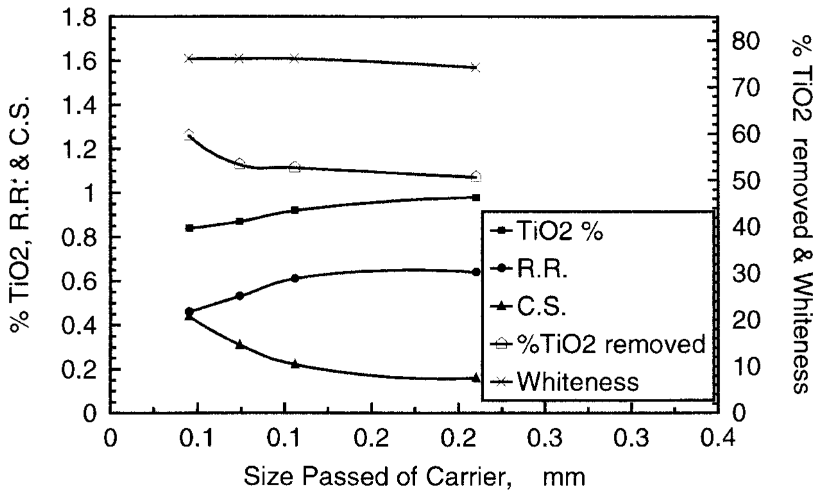

Fig. 2. Effect of grain size of the carrier. Amount of carrier 83.33 kg/ton, sodium silicate 1kg/ton, oleic acid 1kg/ton, pH 10.5, conditioning time 20 min

Classification of the finer size fraction (–0.045) into its sub-sieve sizes showed a further improvement in the grade of the obtained concentrate where the TiO_2 content was decreased to 0.61%, with improving the whiteness to about 90, when the size fraction –25 +10 μm was used as a carrier. At such conditions the C.S. reached its highest value (~0.46) while that of R.R. reduced to its minimum value (0.40) (Fig. 3).

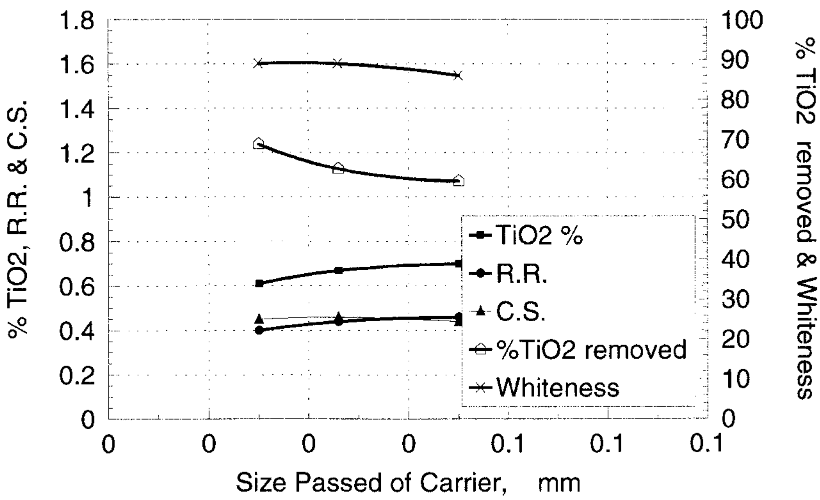

Fig. 3. Effect of grain size of the carrier in the sub-sieve range. Amount of carrier 83.33 kg/ton, sodium silicate 1kg/ton, oleic acid 1kg/ton, pH 10.5, conditioning time 20 min

Since aggregation can be expected to occur in the system, the effect of carrier amount and its size on anatase flotation can be explained by considering possible effects of them on the aggregation process itself. Wang and Somasundaran (1980) proposed the following relationship for calcite as a carrier

$$C = aN$$

where C is the pulp density (i.e., amount of solid per cubic centimeter), N is the particle concentration (i.e., number of particles per cubic centimeter), and a represents the weight of individual particles (gm/particle)

Assuming that the particles are spherical, a can be further expressed as

$$a = 4/3\pi r^3 \rho$$

where r is the radius of the particles and ρ is the density of the particle.

Since carrier amount, C, was kept constant, particle concentration, N, would be expected to decrease with increase in particle size raised to the third power. Since collision rate is a function of particle concentration, if carrier size is increased at constant carrier amount, collision rate can be expected to decrease and this in turn can be expected to lead to a decrease in anatase removal in the form carrier–anatase aggregates (Wang and Somasundaran,1980)

Probability of effective aggregation is governed also by the rate of breakdown of aggregates. The rate of de-aggregation is known to be dependent upon stirring speed and particle size. When particles larger than a particular size limit are used as carrier, the shear force can break down the aggregates especially at very high speed and effective aggregation will thus be negligible. It is likely that such de-aggregation is responsible for the relatively high TiO_2 content (≈ 0.98–0.92%) when the size of the carrier is increased to –0.21 +0.106 and –0.106 +0.074 mm.

CONCLUSIONS

The carrier flotation technique can be successively applied for separation of anatase impurities from a kaolin pre-concentrate. In this technique the amount and grain size of the carrier could determine the performance of the flotation process. These carrier particles increase the aggregation rate of carrier–anatase aggregates, instead of anatase–anatase ones in its absence, thereby facilitating their rate of collision with air bubbles and consequently improve the efficiency of the flotation process. Moreover, the long conditioning time (35 min) required in conventional froth flotation can be significantly reduced to 20 min in the carrier flotation technique. Such reduction in conditioning time will decrease the power consumption needed for the process.

The best conditions for carrier flotation of kaolin are 83.3 kg/ton of limestone with grain size of –25 +10 μm, an impeller conditioning speed 2500 r.p.m., impeller flotation speed 2000 r.p.m., conditioning time of pulp with sodium silicate and oleic acid 25 and 20 min respectively, pH 10.5, and dosage of each of sodium silicate and oleic acid 1 kg/ton. Application of these conditions for upgrading of kaolin gave a concentrate of 0.61% TiO_2 only with a degree of whiteness ~ 90 from a feed containing 1.52% TiO_2. This grade of concentrate is better than that obtained before with conventional froth flotation (0.68% TiO_2 with a whiteness of 78).

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Abdel-Khalek N.A., Hassan F., Arafa M.A., Flotacja noœnikowa egipskiego kaolinu o ultradrobnym uziarnieniu. *Fizykochemiczne Problemy Mineralurgii*, 32, 265–273 (w jêz. angielskim)

Celem tej pracy jest określenie możliwości zastosowania flotacji nośnikowej do usuwania anatazu występującego w egipskich wstępnych koncentratach kaolinowych o uziarnieniu ~80% ziarn poniżej 2 μm, aby koncentrat ten mógł być odpowiedni do produkcji papieru i ceramiki ozdobnej. W badaniach zastosowano krzemian sodu jako depresant i kwas olejowy jak kolektor. Jako nośnika użyto wapnia. Wyniki okazały, że rozmiar ziarn nośnika determinuje efektywność badanego procesu flotacji nośnikowej a znaczny wzrost jakości koncentratu otrzymano poprzez zmniejszenie rozmiaru ziarn nośnika. Zawartość procentowa TiO_2 malała do minimum tj. do 0.6% w porównaniu do 1.52% w nadawie, gdy użyto nośnika o wymiarach ziarn –25 +10 μm. Przy optymalnym rozmiarze ziarn nośnika stopień białości kaolinu osiągał najwyższą wartość (90) w porównaniu do 56 dla nadawy. W tym samym czasie ilość nośnika we flotacji nie miało wpływu na jakość produktu końcowego. Wyniki badań pokazały, że proces flotacji nośnikowej może dostarczyć koncentratów o zawartości TiO_2 podobnej do zawartości w koncentratach otrzymywanych we flotacji pianowej w obecności octanu wapnia jako aktywatora ale flotacji nośnikowa ma tę przewagę, że redukuje długi czas agitacji pulpy z reagentami przy wzbogacaniu konwencjonalnym. Przedyskutowano również mechanizm flotacji nośnikowej.