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# UPGRADING OF MONTMORILLONITE CLAYSTONE FROM WADI BASHIRA, WEST IRAQ, BY CARRIER FLOTATION

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## ABSTRACT

Carrier flotation was applied to upgrade low grade montmorillonite claystone from Wadi Bashira deposit, Western Desert, Iraq, wherein calcium carbonate represent the main impurity.

In this study, polymeric particles were used as carrier materials and the effect of different parameters (oleic acid concentration for pretreatment of carrier particles, pulp-carrier particles contact time, pulp solid concentration and carrier amount) on the efficiency of the beneficiation process were investigated. This was followed through the measurement of CaO content of the treated claystone. According to the test results, an optimum operating parameters were established 15% solid concentration, 4% oleic acid concentration, 4:1 carrier particles: solid in pulp and 15 min contact time. At these conditions montmorillonite clay concentrate containing 2.5% CaO was achieved from about 14% CaO in the untreated sample. Subsequently, the CEC was enhanced, it increased from (60 – 89) meq/100g.

# رفع رتبة أطيان المونتمورلونايت من منطقة وادي بشيرة، غرب العراق، بطريقة التعويم التحميلي

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**المستخلص**

تم استعمال عملية التعويم التحميلي لرفع رتبة أطيان المونتمورلونايت لمنطقة وادي بشيرة الواقعة في الصحراء الغربية، العراق، وتمثل كاربونات الكالسيوم (الكالسايت) المادة الأساسية للشوائب المصاحبة لهذه الأطيان.

استخدمت حبيبات بلاستيكية كمواد حاملة وتم دراسة العوامل المؤثرة على عملية التعويم التحميلي (تركيز حامض الأوليك لتهيئة الحبيبات، زمن التماس اللازم للحبيبات مع اللباب، النسبة المئوية للصلب في اللباب وكمية الحبيبات الحاملة) على كفاءة عملية التركيز. تم متابعة العملية من خلال قياس نسبة CaO في الطين الناتج من العملية. أظهرت نتائج التجارب المختبرية والمنضدية إن الظروف المثلى لعملية التعويم التحميلي هي: 15% نسبة الصلب، 4% تركيز حامض الأوليك، 1:4 نسبة الحبيبات: الصلب في اللباب و15 دقيقة زمن التماس. وعند هذه الظروف تم الحصول على أطيان مونتمورلونايت تحتوي على 2.5% CaO مقارنة بمحتوى الخام 14% CaO، كما تم تحسين سعة التبادل الأيوني من (60 – 89) ملي مكافئ/100غم.

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## INTRODUCTION

Montmorillonite is the most abundant species of the smectite clay mineral group, with a layer structure of 2:1. It is the main mineral comprising fuller's earth and bentonite deposits. Montmorillonites are generally classified as sodium ($Na^+$) or calcium ($Ca^{2+}$) types, depending on the dominant exchangeable cations. It has diverse applications in many areas; like agriculture, drilling operations, paints, cosmetics, foundry, decolorization of oils and many else (Grim, 1968 and Bala *et al*., 2000). In most of these applications, uses of montmorillonite are the consequence of its properties like plasticity, swelling, ion exchange, thixtropy and composition.

In Iraq, low grade calcium based montmorillonite claystone is present in many localities. The deposit located in Wadi Bashira in the Western Desert is considered the biggest deposit ever explored in Iraq. The reserve was estimated (on category C1 and B) by about 300 million tons, averaging 68% montmorillonite associated with attapulgite and non-clay minerals; such as calcite, quartz, gypsum, apatite and halite. Calcite ($CaCO_3$); however, represents the major of these impurities. It is averaging about 15 wt% of the claystone deposit (Al-Bassam and Saeed, 1989). This, besides other impurities detract from the value and utility of the claystone in many applications (drilling mud, foundry, bleaching, refining …etc).

Hora (1998), claimed that montmorillonite deposit (contain ≥ 80% montmorillonite) with less than 10% of impurities is considered as commercially viable deposit, other properties depend on specifications for technical uses. Thereupon, the montmorillonite claystone has to be processed and upgraded to enhance its physical and chemical composition, as well as its economical value. Several beneficiation techniques were practiced, such as dispersion – sedimentation (Song *et al*., 2005 and Al-Ajeel and Abdullah, 2008) acid leaching (Hassan and Abdel-Khalek, 1998, Mhamdi *et al*., 2009 and Al-Ajeel *et al*., 2001), and selective mining (Ainsworth *et al*., 1994).

In this work, carrier flotation was adopted for the beneficiation of the claystone and separation of mineral impurities (particularly calcite). It has been well known that conventional flotation techniques become inefficient for beneficiating fines and ultrafine, such as feed comprising particles passable through a 200 mesh screen (– 75 µm), and particularly those of – 10 micron or finer (Ho *et al*., 1980, Meyer and Jakubowski, 1985 and Abdel-Khalek *et al*., 1998). Such very fine particles may be naturally occurring constituents of a mineral or ore; or may be artificially produced during the grinding of these materials to a suitable size for mineral liberation.

According to this concept, montmorillonite is one of these materials; it is a naturally occurring fine mineral, consisting predominantly of – 2 µm particles (Grim, 1962). Wadi Bashira montmorillonite clay deposit, however, is also mechanically associated with very finely divided impurities (mainly calcite). An effort to remove the calcite by conventional flotation was inefficient (Al-Ajeel *et al*., 2001). In this practice, the fine particles of montmorillonite clay were carried into the froth (either due to entrainment in the liquid or mechanical entrapment within the calcite particles being floated), which led to a large amount of montmorillonite loses. The large surface area of the fine particles resulted also in excessive collector consumption and adversely affected the operation economy. The montmorillonite clay concentrate contains at best no less than 8% CaO. An alternative effective method of beneficiation by flotation of the minerals in fine ore pulps is the carrier flotation.

Many works have been reported on carrier flotation in removing impurities from kaolin, and beneficiating fine minerals from finely divided mineral ore pulp (Collins and Read, 1971, Clark and Windle, 1975, Ho *et al*., 1980, Rubio and Hoberg, 1993, Hu *et al*., 1994, Chia and Somasundaran, 1983, Meyer and Jakubowski, 1985, Valderrama and Rubio, 1998, Abdel-khalek *et al*., 1998 and Lu *et al*., 2005). Carrier particles of various minerals or materials have been used or tested; such as calcite, apatite, scheelite and polymeric particles (Lu *et al*., 2005). However, the first successful commercial application of carrier flotation was reported for removing anatase from kaolin as early as 1961 using calcite particles as carrier particles (Wang and Somasundaran, 1980). In this work carrier flotation was applied for the beneficiation of Wadi Bashira montmorillonite claystone, using plastic carrier particles.

## MATERIALS AND METHODS

Ca-montmorillonite claystone sample from Wadi Bashira region, Western Desert, was collected from many trenches in the deposit for the purpose of this work. The raw sample; as received consisted of a very wide size range (from 12.5 cm to a fraction of centimeter). Some lumps of calcite ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$) were hand sorted and, a homogenized specimen of 1 Kg each having minus 1 cm particle size was then prepared by successive crushing, screening, and dividing.

Polymeric spheres (plastic spheres) of uniform particle size (3 mm) having a density of 0.67 g/cm$^3$ were used as a carrier material in the flotation tests. The spheres were supplied by Al-Furat State Co., Ministry of Industry and Minerals, Iraq. Laboratory grade oleic acid and sodium hydroxide from PDH were used as a collector and pH adjustment, respectively.

To enhance the interaction (hydrophobic interaction) between the calcite mineral and carrier particles, the plastic particles were coated with oleic acid (collector) before use in the flotation process. This was done by mixing the particles with emulsified oleic acid for 5 min, and then screened on a proper sieve to drain the excess acid. Emulsification of oleic acid was performed to enhance its adsorption kinetics at the carrier surface so that, the particular mineral or minerals are preferentially adsorbed on the surface of the carrier (Rubio and Hoberg, 1993).

Slurry (pulp) of raw montmorillonite clay was prepared by high shear mixing of a predetermined weight of the claystone and water. The slurry was then allowed to pass through 200 mesh (75 µm) sieve to remove over size (+ 75 µm) materials. Flotation was then performed in 1 liter plastic container, supplied with three blades stainless steel stirrer. The feed (clay pulp) was put into the container, and its pH was adjusted at 10.5 by NaOH (Antti and Forssberg, 1989 and Abdel-Khalek *et al*., 1998). The carrier particles, which have been coated (pretreated) with oleic acid were then added and mixed at 1500 rpm for a certain time. The separation of the carrier particles was then effected by its low density which floats rapidly up to the pulp surface as the stirring is stopped. The separated carrier particles were washed with water to remove the attached materials, and then agitated with 1N sodium hydroxide solution for short time. The carrier particles were then filtered, dried and reused thereafter. The purified montmorillonite clay pulp was dewatered, dried and analyzed for CaO content.

## RESULTS AND DISCUSSION

### ▪ Characterization of Raw Montmorillonite Claystone Sample

The montmorillonite claystone of Wadi Bashira deposit is of low grade calcium based, belongs to the lower part of the Digma Formation (Late Cretaceous) and it is of a marine sedimentary origin (Al-Bassam and Saeed, 1989).

However, the mineralogical, chemical compositions and CEC of the montmorillonite claystone sample used in this work are shown in Table (1). It indicates that, montmorillonite is the abundant clay mineral and calcite is the major non-clay mineral impurity. Other minerals present are; palygoreskite, quartz, and gypsum. From the chemical analysis, it can be seen that, the claystone sample contains high CaO content (about 14%), which is mainly related to the abundance of calcite ($CaCO_3$) and to some extent to gypsum ($CaSO_4.2H_2O$); as well as the calcium ions associated with montmorillonite structure. According to the value of $SO_3$ given in Table (1), the amounts of gypsum present in the claystone is about 6%, and this accountable for about 2% CaO. The presence of $Na_2O$ and Cl indicate that the claystone contains some halite (NaCl) too. The CEC was found to be about 60 meq/100gm and it indicates a montmorillonite amount of 61.8%.

Table 1: Mineralogical and chemical composition of the investigated claystone sample

| Mineralogical composition | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| montmorillonite, calcite (major), quartz, palygoreskite and gypsum (minor) | | | | | | | | | | | | |
| Chemical Composition (wt%) | | | | | | | | | | | | |
| **$SiO_2$** | **$TiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **CaO** | **MgO** | **$SO_3$** | **$Na_2O$** | **$K_2O$** | **Cl** | **$P_2O_5$** | **L.O.I** | **CEC (meq/100g)** |
| 43.92 | 0.65 | 11.8 | 3.45 | 13.9 | 3.0 | 3.5 | 1.19 | 0.44 | 0.94 | 0.46 | 15.95 | 60 |

According to what have been displayed in Table (1), it becomes clear that calcite represents the predominant non clay mineral impurity and that this investigation seeks for its possible removal (or minimization) from the montmorillonite claystone by carrier flotation. The efficiency of the process; however, was followed through the determination of the CaO content of the upgraded clay produced from the variable experimental tests. The cation exchange capacity (CEC) of the raw claystone, as determined by the methylen blue method (Schenning, 2004), was 60 meq/100g.

### ▪ Effect of Oleic Acid Concentration

Figure (1) shows the results of carrier separation efficiency of calcium-bearing minerals (particularly calcite) from raw montmorillonite claystone represented by CaO% as a function of oleic acid concentration used for pre-treatment of the carrier particles. The data were gained from the carrier flotation experiments, which were performed at the conditions: pH 10.5, pulp solid concentration 6 wt%, amounts of carrier particles: solid in pulp 4:1 by weight, and 5 minute mixing time. It can be realized from Fig.(1) that the carrier flotation accomplished a significant removal of calcite, which can be seen from the dramatic reduction in CaO content of the clay.

The efficiency of the separation process, however, was enhanced by the concentration of the oleic acid. As it can be seen from Fig. (1), the CaO content of the treated claystone was decreased as the oleic acid concentration increases. The lower value of CaO obtained was about 4%, when 4% oleic acid concentration was used. In this respect, the efficiency of the separation (percentage removal of CaO from the starting material), can account by about 71%. Further increase in the oleic acid concentration does not show a significant effect on the separation efficiency of the carrier flotation process. The effect of oleic acid concentration in this experiment was in agreement with the work demonstrated by Wang and Somasundaran (1980); Antti and Forssberg (1989) and Rubio and Hoberg (1993), when flotation separation of calcite from ore pulp was conducted. It seems that at 4% oleic acid concentration, a sufficient residual amount (optimum) of oleic acid from the carrier particles hydrophobize the calcite mineral during agitation, thereupon their interactions increases and removed through carrier flotation.

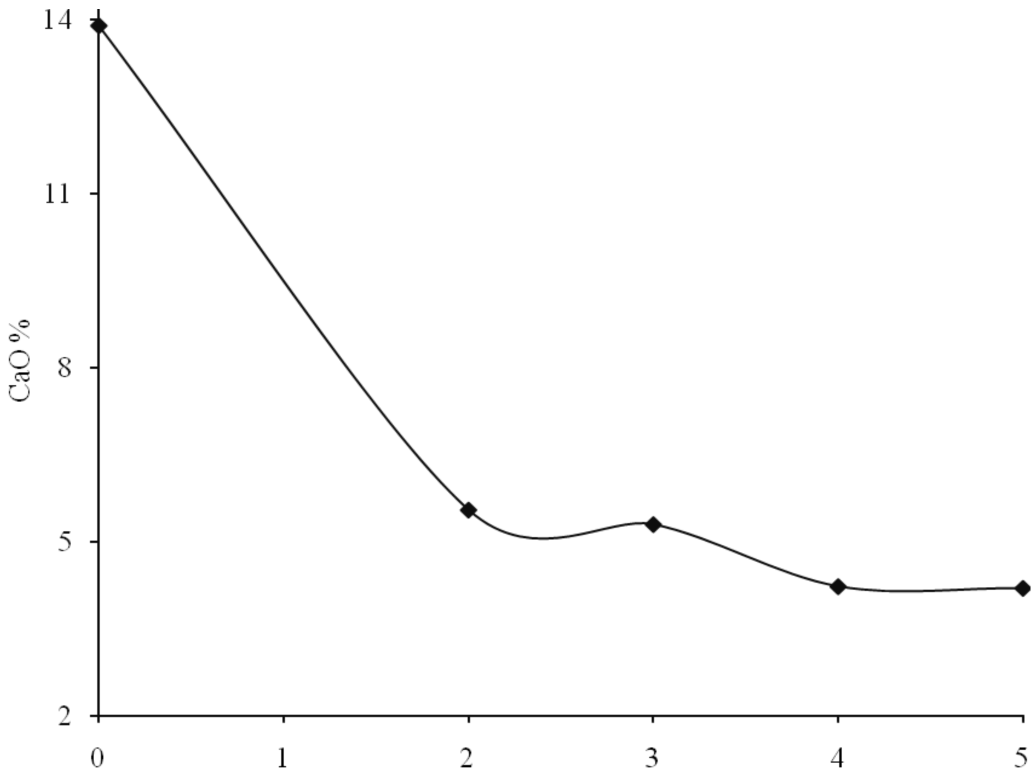


Fig.1: Effect of olic acid concentration on calcite separation

▪ **Effect of Pulp and Carrier Particles Contact Time**

If interaction between the particular mineral and carrier particles is a governing phenomenon, then contact time can be expected to exert a measurable influence on the performance efficiency of the carrier flotation process. In this context, it was found that the CaO content of the treated montmorillonite clay was substantially decreased as the contact time of the pulp and the carrier particles (pretreated with 4% oleic acid) was increased from (5 – 15) minutes. No significant reduction in CaO content was noticed as the contact time increased to 20 minutes, as shown in Fig. (2). The increase in the efficiency of the carrier flotation separation with contact time can be attributed to the increase of calcite particle adsorption for oleic acid collector, which in turn enhance the probability of their adhesion to the surface of the carrier particles. Thereupon, the separation of calcite from the claystone pulp is significantly improved (lower CaO% was obtained). In this set of experiments, a CaO value of 2.8% was achieved in 15 minutes contact time.

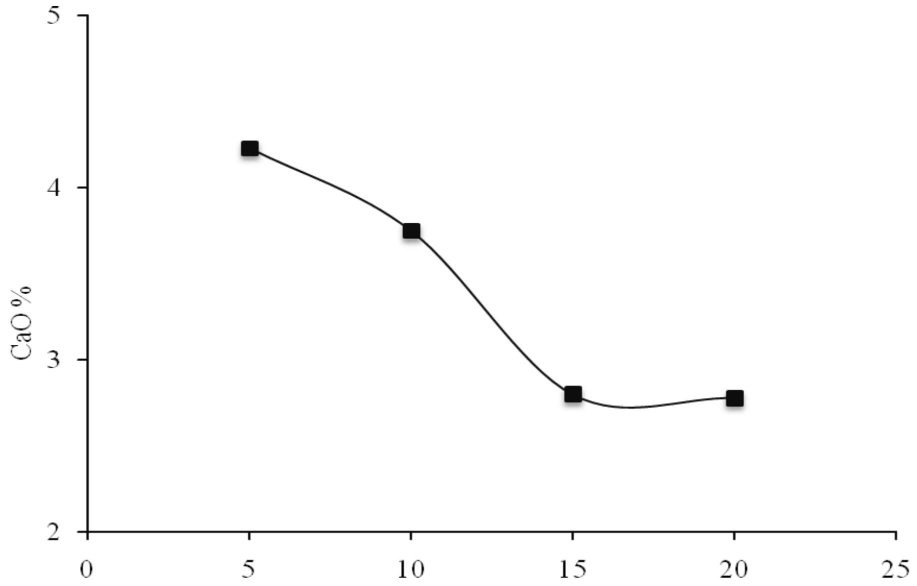


Fig.2: Effect of contact time of the claystone pulp with carrier particles on calcite separation

**▪ Effect of Pulp Solid Concentration**

After optimizing the oleic acid concentration (4%) for the pretreatment of the carrier particles and their contact time (15 minute) with the claystone pulp, the effect of pulp solid concentration on separation of calcite was next studied. The change in pulp solid concentration from (6 – 20) wt% on calcite separation and hence on the CaO content of the yielded material is illustrated in Fig. (3). All flotation tests of this set of experiments were performed at the conditions 4% oleic acid, 15 minute pulp – carrier particles contact time and 4:1 by weight carrier particles: pulp solid content. It is clear from Fig. (3) that, the increase in pulp solid concentration does not produce a significant improvement in the carrier separation process. The CaO content of the yielded clay was reduced from 2.8 to 2.5 and 2.45% as the solid concentration of the pulp increases from 6, 10 and 15 wt%, respectively. The CaO% is slightly increased once again as the pulp solid concentration raised to 20 wt%. In these experiments, it was noticed that in 20 wt% pulp solid concentration the material (carrier particles and claystone pulp) acquire a thick consistency, and a high stirring force was implemented to do the mixing. This property was a major obstacle to smooth separation of the carrier particles from the pulp. Therefore, it is suggested that a pulp solid concentration of (10 – 15) wt% is more convenient for smooth flotation performance.

**▪ Effect of Carrier Amount**

The effect of carrier particles amount used in the flotation was investigated. Ratios of 2:1 and 3:1 by weight of the carrier to the amount of montmorillonite clay in pulp were tested. The results obtained as well as those of 4:1 ratio used in the previous tests are presented in Fig. (4). It can be noted from Fig. (4) the CaO% of the treated clay is inversely proportional to the ratio of the carrier to that of the clay weight.

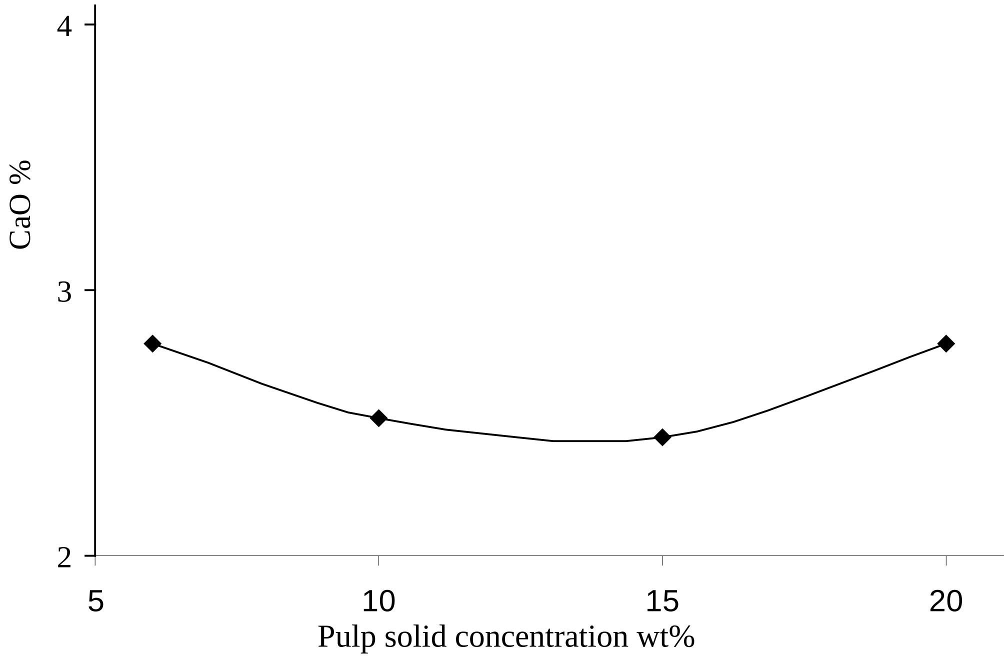


Fig.3: Effect of pulp solid concentration on calcite separation

To ensure the above laboratory findings, a duplicate bench scale carrier flotation experiments were performed, using 3 Kg montmorillonite claystone sample. The operating conditions applied in these experiments were; pH 10.5, pulp solid concentration 15 wt%, oleic acid concentration for the pretreatment of carrier particles 4%, amount of carrier particles: solid in pulp 4:1, and 15 minute stirring time at 1500 rpm. The chemical analysis of CaO in the yielded clay, which was found to be 82% of the feed weight showed that, the CaO of these samples (duplicate) are 2.5 and 2.45%. These results show that the carrier flotation (using polymeric particles) can substantially reduces the CaO content of Wadi Bashira montmorillonite clay and improves its grade, as compared with the conventional flotation. The CaO value was reduced from about 14% in the raw claystone to about 2.5% in the treated sample. In contrast to the conventional flotation of the claystone, CaO content lower than 8.5% could not be achieved (Al-Ajeel *et al*., 2001).

The chemical composition of the upgraded montmorillonite clay by the carrier flotation at the optimum conditions (15% solid concentration, 4% oleic acid concentration, 4:1 carrier particles: solid in pulp (by weight) and 15 minute contact time) was shown in Table (2). As it can be seen, the CaO% in the upgraded clay is about 2.5% compared with about 14% in the raw sample (Table 1), indicating a substantial large removal of calcite. The $Al_2O_3$ content in the concentrate was increased to about 16.8%, as compared with about 11.8% in the raw claystone. The CEC was also increased from 60 meq/100g in the raw to 89 meq/100g in the concentrate, which indicates that the amount of the upgraded montmorillonite clay is highly increased. It increased from (61.8 to 87) %.

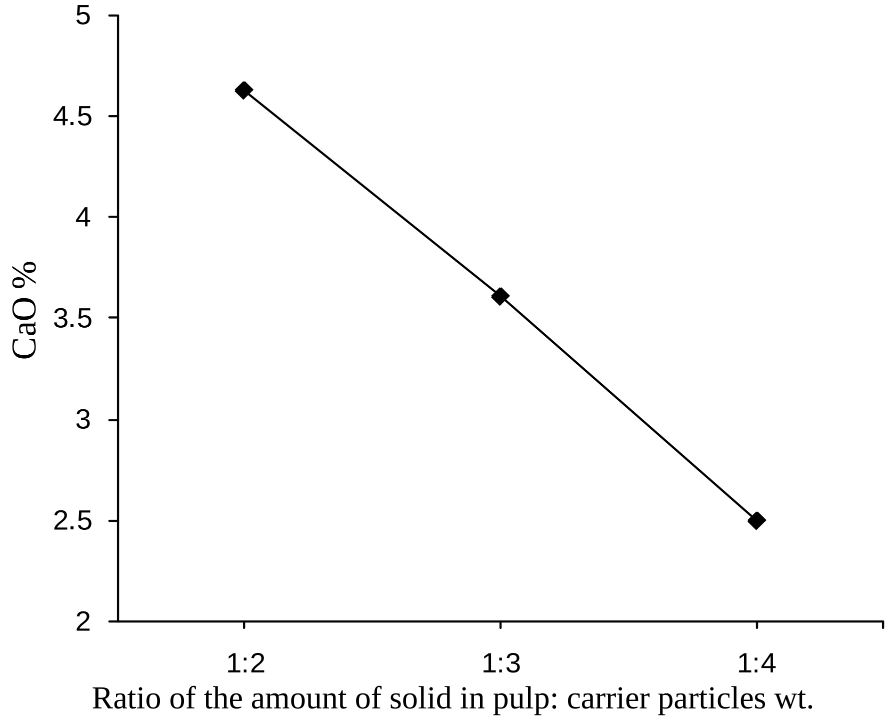


Fig.4: Effect of amount of carrier particles on calcite separation

Table: 2 Chemical composition of the of the upgraded montmorillonite clay

| Chemical Composition (wt%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **$SiO_2$** | **$TiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **CaO** | **MgO** | **$SO_3$** | **$Na_2O$** | **$K_2O$** | **CEC (meq/100g)** |
| 55.0 | 0.7 | 16.8 | 4.54 | 2.5 | 4.7 | 0.4 | 1.16 | 0.53 | 89 |

**CONCLUSIONS**

From the laboratory and bench scale experimental results, the following conclusion can be made:

- Carrier flotation technique using plastic particles as a carrier and oleic acid as collector, can be successfully applied for the separation of calcite for the beneficiation of Wadi Bashira montmorillonite claystone.
- The concentration of the oleic acid used for the pre-treatment of the carrier particles and their contact time with the pulp can determine the efficiency of the flotation separation of the calcite.
- Owing to the low density (lower than water) of the carrier (plastic particles), flotation separation is very rapid and allows an easy removal from the pulp.
- Detachment of collected calcite particles from the surface of the carrier was very easy, using normal agitation with sodium hydroxide solution.
- Montmorillonite clay of very low CaO content (2.5%) can be achieved by the carrier flotation using the following conditions: pH 10.5, pulp solid concentration 15 wt%, oleic acid concentration 4%, amount of carrier particles: solid in pulp 4:1, and 15 minute stirring time at 1500 rpm.

- In this process the yielded clay was found to be 82% of the feed weight.
- This work shows that carrier flotation is indeed more effective for the purification (removal of calcite) of low grade Wadi Bashira montmorillonite clay than the conventional flotation process.

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