

UPGRADING OF MONTMORILLONITE CLAYSTONE (DIGMA FORMATION) FROM WADI BASHIRA, WESTERN DESERT, IRAQ

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ABSTRACT

Wet beneficiation processing of Wadi Bashira Ca-montmorillonite claystone, which belongs to the Digma Formation, has been studied using tetrasodium pyrophosphate as dispersant agent. The claystone is located in the Western Desert of Iraq. It is of a low grade, associated with different amount of clay and non-clay mineral impurities. Calcite (CaCO_3) constitutes the major proportion of these impurities.

In this study, the effect of different parameters (slurry solid concentration, dispersant amount and dispersant/ slurry mixing times) on the efficiency of the beneficiation process were investigated and followed through the measurement of $\text{CaO}\%$ values of the upgraded claystone (concentrate). Gravity and centrifugal sedimentation were tested to separate the impurities from the clay suspension. The process variables were optimized and the yielded claystone was evaluated. It was shown that the beneficiation process was very effective in upgrading the montmorillonite claystone and capable of producing a high grade montmorillonite (89% montmorillonite) with CEC of 85 meq/100 gm.

رفع رتبة أطيان المونتمورلوناييت (تكوين دگمة) من منطقة وادي بشيرة،
الصحراء الغربية، العراق

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المستخلص

تمت دراسة عملية التركيز الرطب لأطيان المونتمورلوناييت الكالسيومي لوادي بشيرة باستخدام ثلاثي صوديوم بيروفسفات كمادة مشتتة. يقع راسب الطين المستخدم في هذه الدراسة ضمن تكوين دگمة في الصحراء الغربية من العراق وهو من الأنواع واطنة النوعية ويرتبط مع كميات مختلفة من الشوائب المعدنية، الطينية وغير الطينية وتمثل كاربونات الكالسيوم الجزء الأكبر من هذه الشوائب.

تم البحث في هذه الدراسة، تأثير العوامل المختلفة (المتتمثلة بتركيز المواد الصلبة في اللباب (خليط الطين والماء)، كمية المادة المشتتة وزمن مزج المادة المشتتة مع اللباب) على كفاءة عملية التركيز ومتابعتها من خلال قياس نسبة CaO في ركاز الطين الناتج. وقد درست عمليتي الترسيب الطبيعي والطرء المركزي في مرحلة فصل الشوائب عن الأطيان التي هي في حالة عالق، نتيجة لتأثير المادة المشتتة.

بعد تحديد القيم المثلى للمؤشرات الفنية لعملية التركيز وتقييم ركاز الطين الناتج من خلال التحاليل الكيميائية ونسبة المونتمورلوناييت وسعة التبادل الأيوني، لوحظ ان عملية التركيز كانت كفوءة جداً في رفع رتبة الطين، وأدت الى إنتاج نوعية عالية من أطيان المونتمورلوناييت، تصل نسبة المونتمورلوناييت فيها الى 89% وسعة التبادل الأيوني بحدود 85 ملغم مكافئ لكل 100 غم خام.

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INTRODUCTION

Montmorillonite occupies a prominent position among industrial minerals. It is the main constituent of bentonite and the detrimental factor of its properties. Regardless of origin or occurrence, montmorillonite and bentonite are two names of exactly the same mineral (Grim, 1968).

Montmorillonite belongs to smectite class of clay minerals, which has 2:1 type of layer structure. Meaning that each layer consists of three sheets, an octahedral alumina sheet sandwiched between two tetrahedral silica sheets (Grim, 1968; Ainsworth *et al.*, 1994 and Schenning, 2004). Because of the isomorphous substitution of Mg^{2+} and/ or Fe^{2+} for Al^{3+} in the octahedral sheet and Al^{3+} for Si^{4+} in the tetrahedral sheet, the particle of montmorillonite is negatively charged at the surface and positively charged at the edges. The electrical neutrality is attained by other cations (external to the lattice) that reside in the inter-laminar region, between the lattice layers. These cations (usually Na^+ or Ca^{2+}) are relatively easily exchangeable, giving montmorillonite high cation exchange capacity phenomenon (Grim, 1968; Ainsworth *et al.*, 1994; Bala *et al.*, 2000 and Schenning, 2004). The type of cation that fulfils the charge-balancing role has marked impact on the performance of the montmorillonite in terms of its capacity for swelling, thixotropy, and adsorption (Grim, 1962 and Ainsworth *et al.*, 1994). In industry, montmorillonite is generally either sodium (Na^+) or calcium (Ca^{2+}) type. Sodium montmorillonite, where the inter-laminar region is occupied mainly by sodium ions (dominant exchangeable ion), has very high swelling capacities and thixotropic properties when added to water, therefore, it is highly valuable as drilling muds and other uses requiring thixotropic suspension. The Ca-montmorillonite has no value for such application. It has a very little swelling ability; flocculation and settling are much more rapid than for sodium montmorillonite (Keren, 1988; Bowyer and Moine, 2008 and Alther, 2004). Therefore, this type is directed largely for bleaching of oils (Grim, 1962).

In Iraq, particularly in the Western Desert, montmorillonite was first reported in 1985 by Al-Bassam and Al-Saadi (1985). Years later, the exploratory works of Khdaire and Al-Saady (1987) and Al-Bassam and Saeed (1989) resulted in localizing two calcium montmorillonite claystone deposits. The deposit, located in Wadi Bashira (Fig.1), was considered the major deposit explored in the Western Desert. It represents the lower part of the Digma Formation of Late Cretaceous age and of marine sedimentary origin. It is of low grade with montmorillonite content; averaging about 68 wt%, associated with clay and non-clay impurities including attapulgite, calcite, quartz, apatite, gypsum, and halite. These impurities account about for 32 wt% of the deposit. Calcite, however, represents the major impurity, it averages about 15 wt% of the deposit (Al-Bassam and Saeed, 1989). This montmorillonite claystone deposit, showed a poor response to sodium activation and failed when tested (API specification) for drilling mud (Al-Ajeel *et al.*, 1990).

Generally, the major problems facing the utilization of Wadi Bashira claystone deposit are its low concentration of montmorillonite (about 68%), high level of impurities, and inconsistent composition. Therefore, it has to be processed and upgraded before utilization. The potential method for this purpose is the wet beneficiation method (Ainsworth, 1994).

It has been demonstrated (Hassan and Abdel-Khalek, 1998) that by subjecting Egyptian Ca-bentonite slurry to a hydrocyclone classifier and treating the over flow with dilute HCl, led to effective removal of calcite impurities. The same results were achieved when slurry of Iraqi Ca-montmorillonite claystone was treated with dilute HCl to remove calcite impurities (Al-Ajeel *et al.*, 2003), the same authors also claimed that an effective removal of the calcite gangue could be achieved by carrier flotation (the carrier material used was light polymer beads). Furthermore, it was shown (Shaoxian *et al.*, 2005) that dispersion and sedimentation

processes with sodium phosphate as dispersant was very effective in beneficiating China Ca-montmorillonite claystone. The reject from this process was mainly quartz sand.

It was also reported (Al-Ajeel *et al.*, 2007) that dispersion sedimentation technique with tetrasodium pyrophosphate was very effective in separating carbonate impurities from Iraqi attapulgite – montmorillonite claystone deposit, and the reject was mainly calcite.

The objective of the present work is, to study the beneficiation potential of Wadi Bashira montmorillonite claystone, using dispersion sedimentation method, and to establish the best condition of the process parameters (e.g. dispersant addition, slurry stirring time, slurry solid concentration and centrifugal separation).

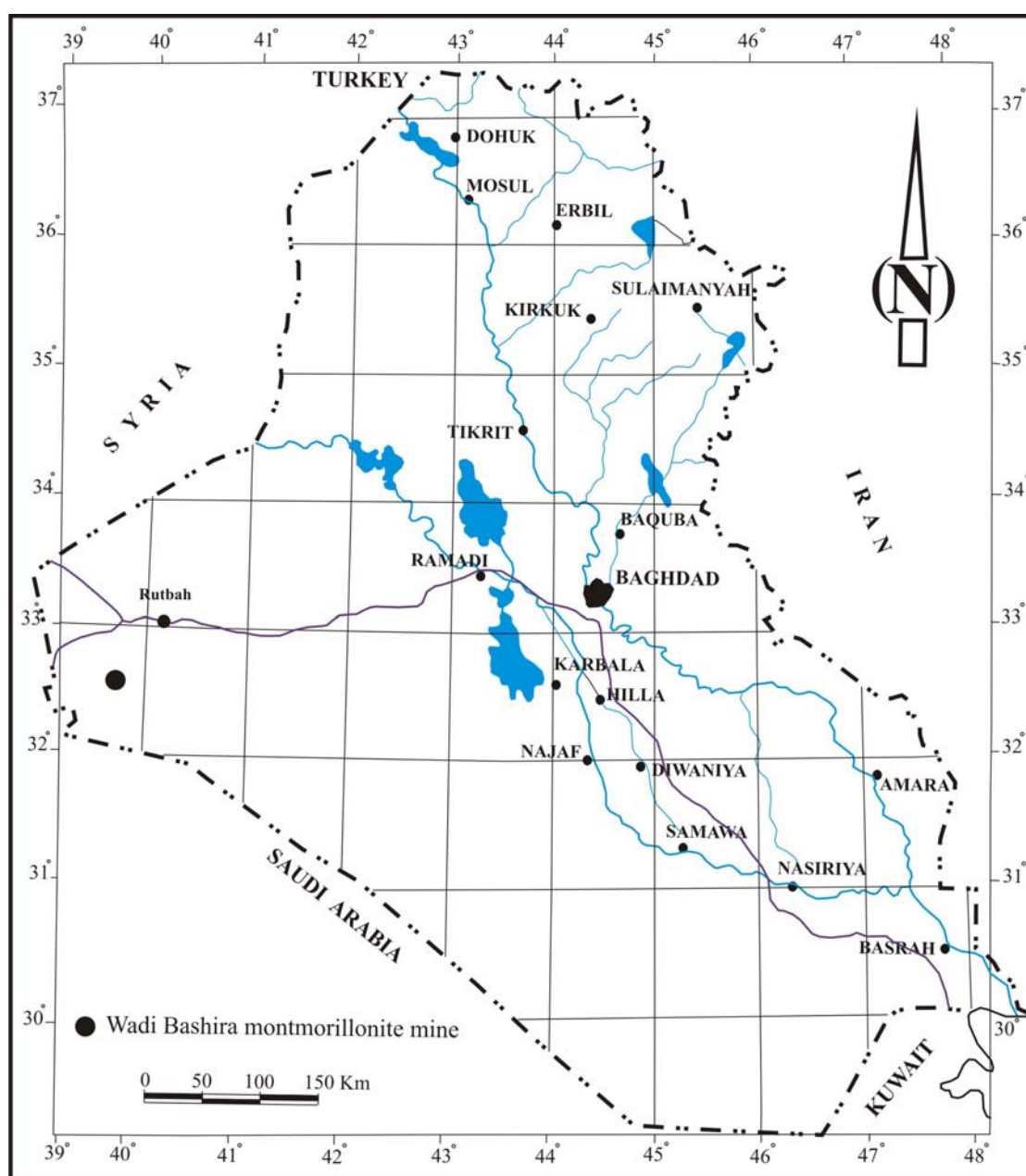


Fig.1: Location map of montmorillonite claystone deposit of Wadi Bashira (Digma Formation) in the Western Desert of Iraq

MATERIALS AND METHODS

Montmorillonite claystone sample of Wadi Bashira collected randomly from many trenches in the deposit was used for the beneficiation tests. The dispersing reagent used was analytical grade tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_{10}\text{H}_2\text{O}$) (TSPP).

▪ Sample Preparation

The claystone sample, as received, was successively crushed to pass 4 mm sieve in a laboratory jaw crusher, then identical samples of 0.5 Kg each were separated for the tests using Jons Riffle sampler. Furthermore, a representative specimen was withdrawn for chemical, XRD and cation exchange capacity (CEC) analysis. The CEC, was determined by the methylene blue adsorption method, and was used to evaluate the montmorillonite purity of both, feed sample and the upgraded clay (concentrates). The procedure used was European Standard (Schenning, 2004).

▪ Mineralogical and Chemical Composition

Table (1) presents the mineralogical and chemical composition of the investigated montmorillonite claystone sample. According to the XRD analysis results, the predominant identified minerals were; Ca-montmorillonite, calcite, quartz, kaolinite, and palygorskite (attapulgite), with minor amounts of feldspar. The chemical analysis results display the presence of Cl (1.16%), SO_3 (1.4%) and P_2O_5 (0.4%), which accordingly indicates the association of halite (1.9%), gypsum (3%) and apatite (1.4%), respectively with the claystone raw sample. The data of Table (1) showed a high value of CaO (9.5%) that suggests the presence of high amount of calcite (CaCO_3).

Table (1) Mineralogical and chemical composition of the investigated montmorillonite claystone raw sample

| Mineralogical Composition | | | | | | | | | | |
|--|--------------------------------|--------------------------------|-----|-----|-----------------|-------------------------------|-------------------|------------------|------|-------|
| Montmorillonite, Calcite, Quartz, Kaolinite, Palygorskite (Attapulgite) and Minor Feldspar | | | | | | | | | | |
| Chemical Composition (wt %) | | | | | | | | | | |
| SiO ₂ | Fe ₂ O ₃ | Al ₂ O ₃ | CaO | MgO | SO ₃ | P ₂ O ₅ | Na ₂ O | K ₂ O | Cl | L.O.I |
| 48.56 | 4.48 | 13.16 | 9.5 | 4.6 | 1.4 | 0.4 | 1.13 | 0.32 | 1.16 | 14.22 |

The results of CEC and montmorillonite measurements of the claystone raw sample were about 68.7 meq/ 100 gm and 72%, respectively. It has been reported (Hora, 1998) that economic grade bentonite; usually contains more than 80% montmorillonite. Other properties depend on the specification for particular application. Therefore, in order to improve the grade (purity) of Wadi Bashira montmorillonite claystone, it has to be processed; so that the associated impurities can be removed or reduced. This should enhance the quality of the deposit in terms of CEC value and montmorillonite content.

▪ Upgrading of Montmorillonite Claystone

The employed beneficiation method comprised the following steps:

- Preparing a slurry of the crushed montmorillonite claystone containing 8 wt% solid and then degritting the slurry on 75 μm to remove the over size (+75 μm) fraction.
- Adding dispersant to the degritted slurry to disperse the clay in water.
- Separating the dispersed clay from undispersed (settled) material by decantation after;
a) gravity sedimentation and, b) centrifugal sedimentation.

- For gravity sedimentation, the suspension was left static for (2 – 2.5) hr, and then the clay suspension was separated by decantation.
- For centrifugal sedimentation, different speeds (500, 600 and 700) rpm and times (5, 10 and 15) min were tested.
- Dewatering the decanted dispersed clay at high speed centrifugation.
- Drying the separated clay at $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and then analyzing the dried clay for CaO and CEC.

In this work, the effect of dispersant amount, clay slurry concentration, centrifugal times and speeds on the quality of the beneficiated montmorillonite claystone yielded were tested.

RESULTS AND DISCUSSION

▪ Effect of Dispersant Addition

The effect of the dispersant (TSPP) addition on the upgrading of montmorillonite claystone from the raw sample was investigated through the measurement of CaO% content of the beneficiated claystone. The amount of the dispersant added to the clay slurry varied from (0.5 – 8.5) wt% (at 1% interval) of the dry claystone raw sample. The first series of tests were carried out at conditions of: **a)** 2 wt% slurry solid concentration, **b)** 5 min dispersant mixing time and **c)** gravitation sedimentation to separate the non-clay impurities. Figure (2) illustrates the effect of the dispersant concentration on CaO% value of the upgraded claystone. Generally, it can be seen, that the CaO% value of the montmorillonite claystone concentrate decreases with the increase of the dispersant addition to about 7.5 wt% and the excess of this amount induced a reverse effect. The decrease in CaO value discloses that, the grade of the montmorillonite concentrate is accordingly increased. This was supported by the increase of the CEC of the montmorillonite concentrate (contain 3.34% CaO, at 7.5 wt% dispersant addition), which was found of about (84 – 85) meq/ 100 gm. This suggests that the addition of 7.5 wt% dispersant agent can be considered as optimum value. Beyond this value, it was observed that the viscosity of the slurry slightly increased and led to a bad separation of the non-clay impurities. Consequently, the CaO content of the yielded clay was increased. Furthermore, it was also found that, the addition of less than 4.5 wt% of the dispersant suppresses the clay suspension, and hence high CaO value was obtained.

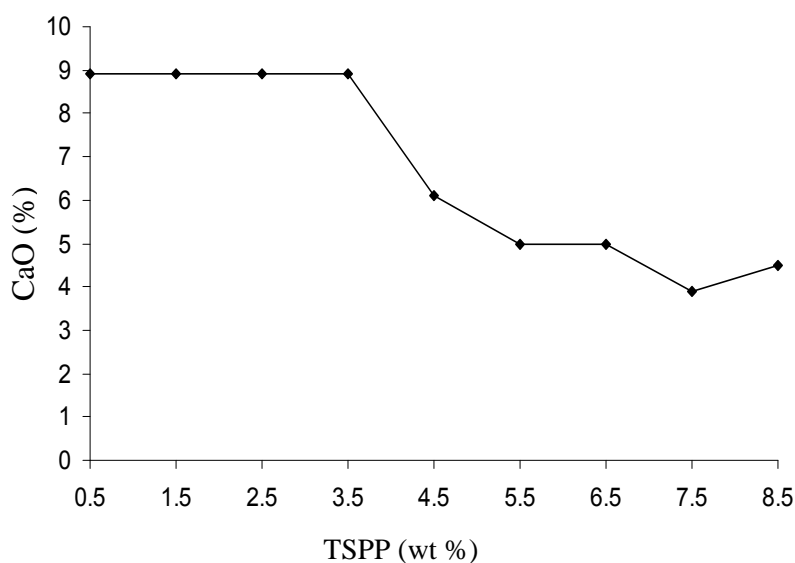


Fig.2: Effect of dispersant dosage on the CaO%

▪ **Effect of Mixing Time**

After optimizing the amount of the TSPP addition (7.5 wt%), the dispersant mixing time was next studied. High rate mixing (1200 rpm) is very beneficial process for wetting of the clay particles and breaks down of the particle – particle linkage, hence allows the dispersant ions to chemisorbed at the edge surface of the clay particles. This procedure would increase the electrical double layer repulsion between the clay particle surfaces; in the slurry and induces its suspension (Keren, 1988 and Shaoxian *et al.*, 2005). The effect of the slurry mixing time in the dispersing step at 1200 rpm and 2 wt% solid on CaO content of the upgraded montmorillonite claystone is shown in Fig.(3). It can be seen from this figure, that increasing the mixing time more than 7 min has no significant effect on the CaO% value of the beneficiated claystone. Therefore, mixing time of 7 min was considered as optimum time for the clay dispersing step.

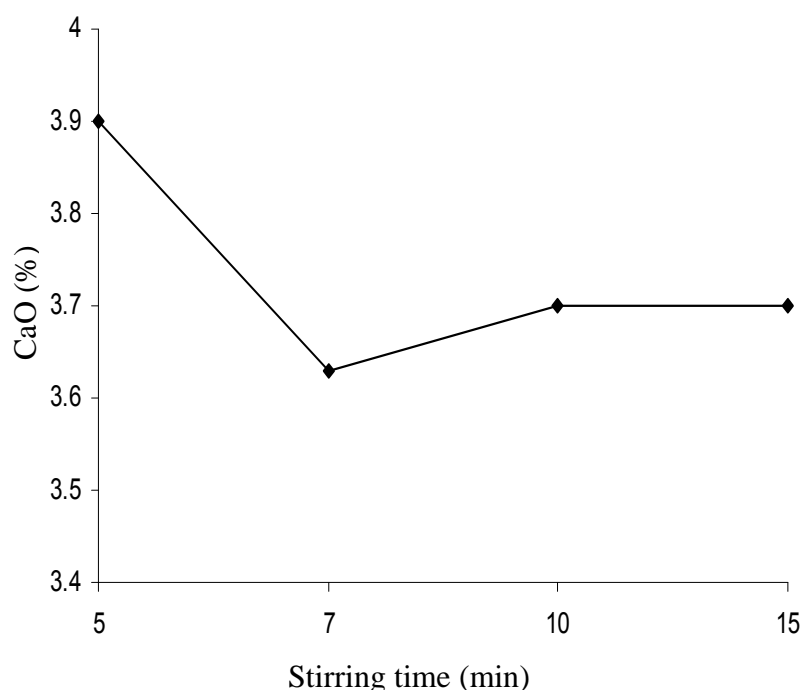


Fig.3: Effect of dispersion stirring time on CaO%

▪ **Effect of Solid Concentration**

The effect of solid concentration (raw montmorillonite claystone concentration) of the slurry in the dispersing step (7.5 wt% dispersant addition with mixing velocity of 1200 rpm for 7 min) on the upgrading operation is represented in Fig. (4). It can be observed from this figure, that the CaO value of the yielded claystone concentrate gradually increases as the solid concentration increases from (2 – 6) wt%, and then sharply increases as the solid concentration increases to 8 wt%. This happened due to a high gel formation and complete compaction of the particles, which can be attributed to the fact that as the proportion of solids in the slurry increases the effect of particles crowding becomes more apparent and the slurry attends a state of high viscosity. In such condition, hindered settling prevails and the falling rate of the particles decreases. Consequently, the sedimentation of fine particles does not occur and the whole beneficiation process obstructed. Anyhow, according to the results obtained, it can be deduced that a successful upgrading of the raw montmorillonite claystone can be only achieved at a solid concentration of (1 – 3) % by weight.

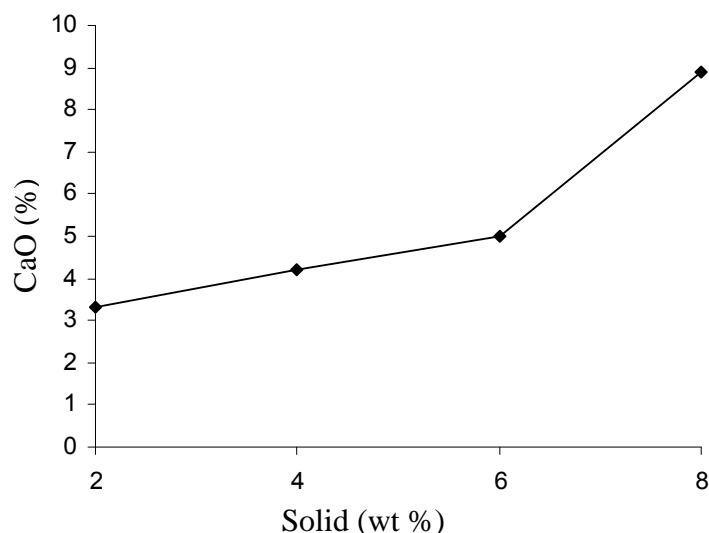


Fig.4: Effect of slurry solid concentration on CaO%

▪ Effect of Centrifugal Sedimentation

Owing to the long time (2 – 2.5 hr) required for the gravitational sedimentation to separate the impurities from the clay suspension, centrifugal sedimentation was next tested at the optimum conditions obtained (7.5 wt% dispersant, mixing time 7 min at 1200 rpm and 2 wt% solid concentration). The results are illustrated in Fig. (5) in the form of CaO percentage of the upgraded claystone as a function of centrifugal time (5, 10 and 15 min) at various speeds (600 and 700 rpm). The tests of using lower speeds (500 rpm) for different times (5, 10 and 15 min) showed very little sediment of impurities, that quickly disbanded (unstable and cannot be separated), therefore it was not considered in the data of Fig. (5). It can be seen from this figure, that the minimum value of CaO (2.7% CaO) in the beneficiated montmorillonite claystone achieved, was at centrifugal speed of 700 rpm for 15 min time. At these conditions, the CEC test result of the obtained montmorillonite claystone was 84.5 meq/ 100 gm, therefore this speed (700 rpm) was considered as optimum for the centrifugal sedimentation operation.

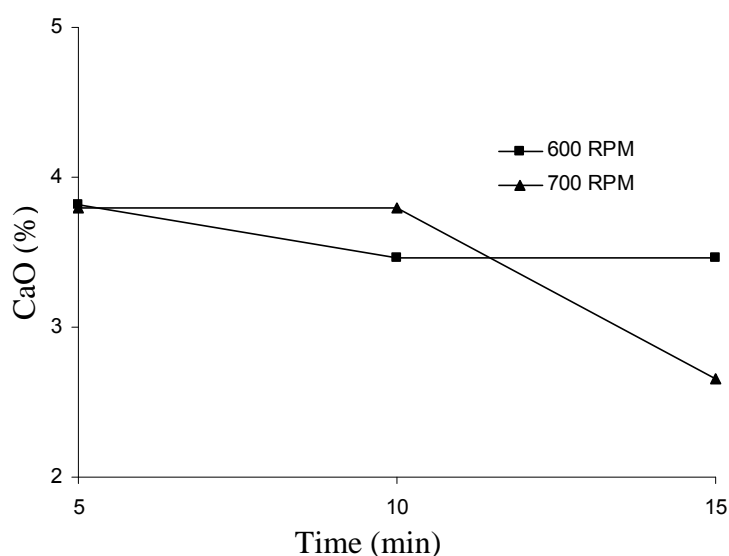


Fig.5: Effect of centrifugal time and speed on CaO %

The chemical composition results of the upgraded montmorillonite claystone, obtained at the optimum conditions (2 wt% solid, 7.5 wt% TSPP, 7 min stirring time and 700 rpm centrifugal speed) with that of the ideal theoretical composition calculated by Al-Bassam *et al.* (2008) are shown in Table (2). It can be noted, that the chemical composition of the upgrading montmorillonite claystone has a fair resemblance to that of the ideal calculated values. Therefore, the upgraded montmorillonite claystone can be considered as a high grade product. The purity was also reflected by the values of CEC and the montmorillonite content, which were found of 84.5 meq/ 100 gm and 89%, respectively.

Table 2: Chemical composition results of the upgraded montmorillonite claystone and the ideal calculated values of the claystone

| Component % | Upgraded montmorillonite claystone | Ideal calculated values of montmorillonite claystone (Al-Bassam <i>et al.</i> , 2008) |
|--------------------------------|------------------------------------|---|
| SiO ₂ | 55.0 | 60 |
| Fe ₂ O ₃ | 5.38 | 5.3 |
| Al ₂ O ₃ | 18 | 20 |
| CaO | 2.66 | 1.6 |
| MgO | 4.6 | 3.3 |
| K ₂ O | 0.55 | 0.5 |
| Na ₂ O | 1.7 | 0.9 |
| SO ₃ | — | — |
| P ₂ O ₅ | — | — |
| Cl | — | — |
| TiO ₂ | 1.54 | — |
| L.O.I | 9.4 | 8.4 |
| Total | 98.83 | 100.00 |

CONCLUSIONS

According to the experimental results of this work the following conclusions can be stated:

- Wet processing of Ca-montmorillonite (Digma Formation) from Wadi Bashira, using tetrasodium pyrophosphate as dispersant was very effective in upgrading the montmorillonite. In this process, a high grade montmorillonite claystone (89% montmorillonite) was achieved with CEC of about 85 meq/ 100 gm.
- Low solid slurry concentration, and optimum dispersant amount are the important parameters in the beneficiation process.
- Gravitational sedimentation of the impurities is very lengthy (2 – 2.5 hr) as compared with the centrifugal sedimentation (10 min) to achieve the same results, with respect to CaO% of the upgraded montmorillonite claystone.
- Centrifugal sedimentation at low to moderate speed is highly effective in separating the impurities from the suspended clay.
- The best beneficiation operating conditions at which a high grade montmorillonite claystone (89% montmorillonite) was obtained were 7.5 wt% TSPP, 2% slurry solid concentrate, 7 min slurry mixing time and 700 rpm centrifugal speed.

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