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BENEFICIATION OF ATTAPULGITE – MONTMORILLONITE CLAYSTONE BY DISPERSION SEDIMENTATION

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ABSTRACT

The beneficiation of attapulgite – montmorillonite claystone has been studied with dispersion sedimentation technique using polyionic salts as dispersant. The study was performed on attapulgite-rich claystone sample from the Digma Formation exposed in the Western Desert of Iraq. The clayey materials mainly consist of attapulgite and montmorillonite minerals, together with quartz, calcite, dolomite and gypsum as impurities. Calcite represents the major impurity associated with the clay. Type and dosage of dispersant (namely sodium hexametaphosphate, and tetrasodium pyrophosphate) and slurry solid concentration were tested to understand their effect on the beneficiated process. The results showed that tetrasodium pyrophosphate was the best for achieving good beneficiation of attapulgite clay from dilute crude slurry.

تركيز أطيان الاتابلغايت والمونتمورلونايت بالتشتيت والترسيب

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المستخلص

تم دراسة عملية تركيز اطيان الاتابلغايت - المونتمورلونايت بطريقة التشتيت والترسيب باستخدام الأملاح الأيونية المتعددة كمواد مشتتة. تم إجراء الدراسة على نموذج من الأطيان الغنية بالاتابلغايت، ملتقط من تكوين الدكمة المتكشف في الصحراء الغربية العراقية. تتكون المواد الطينية أساسا من معدني الاتابلغايت والمونتمورلونايت بالإضافة الى معادن غير طينية (الكوارتز، الكالسايت، الدولومايت والجبسم) كشوائب. ويمثل الكالسايت الشوائب الرئيسية المصاحبة للأطيان. جرت التجارب عند ظروف متغيرة من نوع وكمية المادة المشتتة، وهي ثلاثي متعدد فوسفات الصوديوم وسداسي ميتا فوسفات الصوديوم وتركيز المادة الصلبة في اللباب لغرض معرفة تأثيرها على عملية التركيز. بينت النتائج بان مادة ثلاثي متعدد فوسفات الصوديوم هي الأمثل للحصول على تركيز جيد لأطيان من اللباب المخفف للطين.

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INTRODUCTION

Attapulgite (palygorskite) is a naturally occurring non-swelling clay mineral of needles, fibers or fibrous cluster morphology, it is composed of hydrous magnesium – aluminum silicate, having a theoretical formula of $Mg_5Si_8O_{20}$ $(OH)_2$ $(OH_2)_4$. $4H_2O$, where significant substitution of Mg^{+2} by Al^{+3} and Fe^{+3} occur in the octahedral position and Ca^{+2}, Na^{+} and K^{+} occur as interlayer cations (Grim, 1968 and Al-Bassam, 1998).

Attapulgite is well known as fuller's earth and has been used for many years to decolorize, filter, and refine animal, mineral, and vegetable oils and greases. The clay is an effective absorbent for oil, greases, water and other chemicals. It is also used as drilling mud in salt media (Grim, 1962).

Attapulgite is widely distributed in Iraq, occurring in many rock units, the Digma Formation is one of the important attapulgite-rich formations in Iraq (Al-Bassam, 1998). The attapulgite, in this formation, is of marine sedimentary origin and almost always associated with montmorillonite (Khalid *et al.,* 1997). Other minerals such as quartz, calcite and dolomite are also present. Montmorillonite is layered, hydrated sodium, calcium, magnesium, aluminum silicate. Its general chemical formula is $(M^{+}_{y}$. $nH_2O)$ $(Al_{2-y}Mg_y)$ Si_4O_{10} $(OH)_4$, where M = Na^{+}, Ca^{+2}, Mg^{+2} is the interlayer changeable cations (Brindley and Browan, 1980 and Bala *et al.,* 2000).

The montmorillonite associated with the attapulgite-bearing rocks of Digma Formation is of calcium base. It is non-swelling clay and predominantly classed as fullers earth, similar in this respect to attapulgite. World fuller's earth, however, is generally comprising minerals such as attapulgite (palygorskite) or montmorillonite or a mixture of the two (grades from attapulgite-rich to montmorillonite-rich clays). The attapulgite-rich claystones of Digma Formation were proved to be of industrial value in term of oil wells drilling, decolorizing and absorbing characteristics (Al-Bassam, 1998). As so far mentioned, the attapulgite claystone contains other non-clay minerals (quartz, calcite, gypsum …etc), which were formed in situ or were transported into the deposit during its formation, and these may approach levels of 30 weight percent or more. This motivates the need to upgrade the attapulgite by effective method to enhance both clay performance and commercial value.

It was demonstrated (Maynard *et al*., 1969; Jacobs *et al*., 1971; Trawinsk, 1979 and Prakash *et al*., 2001) that after dispersing the raw clay into slurry of low enough viscosity by certain polyanion dispersing agents, the non-clay materials will settle to the bottom due to gravitational force. The settled materials can then be removed by screening, sedimentation tank, hydrocyclon or other physical separation methods. Wills (1997); Pual *et al*. (2000) and Robert and Dennis (2002) described a process for purifying attapulgite from other clays (kaolinite and montmorillonite) and mineral species by using special type of dispersing agent. According to aforementioned publications the effectiveness of clay wet beneficiation depends largely on the attainment of maximum fluidity or minimum viscosity in the clay – water system that can allow non-clay materials free to settle, in accordance with their size and mass.

The objective of this study is to provide a simplified method for removal of non-clay materials from clay minerals component associated with attapulgite claystone of the Digma Formation employing the principle of dispersion sedimentation concept. Briefly, the work involves treatment of an aqueous claystone slurry with dispersant to impart a high degree of suspension stability to the clay particles at a minimum aqueous viscosity. The settling of non-clay particles then becomes possible and freed from the clay suspension.

EXPERIMENTAL WORK

- **Materials**

Attapulgite-rich claystone sample (50 Kg) from the Digma Formation deposit (Akashat area) was initially prepared by crushing, mixing, quartering and dividing into identical samples. Each loat of sample, weighing about 1 Kg, having particle size of minus 19 mm. Sample from the prepared claystone was drawn for chemical and mineralogical analysis. The results of these analyses are given in Table (1) and Fig. (1), respectively. Tetrasodium pyrophosphate ($Na_4P_2O_7$. $10H_2O$) and sodium hexametaphosphate [Na_6 $(PO_3)_6$] of analytical grade were used as dispersing agents. Tap water was used for clay slurring.

Table 1: Chemical analysis of the crude attapulgite – montmorillonite claystone sample

SiO_2 %	Fe_2O_3 %	Al_2O_3 %	CaO %	MgO %	K_2O %	Na_2O %	SO_3 %	L.O.I %
40.1	3.38	9.6	19.64	4.36	0.29	0.8	0.32	20.5

- **Beneficiation of the Aattapulgite Raw Claystone**

As a first step in carrying out the process of this work, the initially prepared attapulgite raw claystone sample was mixed with water to form aqueous slurry containing 15% solid of raw claystone, on dry weight bases. The claystone slurry preparation experiments indicated that mixing speed of (900 - 1000) rpm for 45 min was sufficient to produce well homogenized clay slurry. Following the conventional practice, by adding the dispersant at the slurring time, it was observed that during the mixing operation the viscosity of the clay – water system is highly increased forming a hydrogel suspension. Therefore, it was decided to add the dispersant in the latest step.

The attapulgite claystone slurry was then degritted by allowing the slurry to pass through 75 or 53 µm to remove over size materials. The degritted slurry was then diluted with tap water to certain slurry concentration (2, 3, 5, 7, 10 and 13) % by weight. Subsequently, sufficient quantity of dispersant was added to achieve substantial high fluidity (low viscosity) clay suspension that permits gravity sedimentation of non-clay fine materials to the bottom of the claystone slurry container. The suspension was allowed to separate into two layers, comprising suspended clay and settled impurities. Next, the suspended clay slurry was separated (by decantation) and subjected to centrifugation to separate the beneficiated clay. The yielded clay was conventionally dried and analyzed for CaO content (CaO content of the beneficiated clay was considered as a function of clay purity). Nevertheless, the effect of the degritted clay solid concentration, dispersant type and dosages on the beneficiation process was studied.

RESULTS AND DISCUSION

- **Mineralogical and Chemical Composition**

According to the mineralogical analysis of the raw claystone sample determined by X- ray diffraction (Fig.1) the predominant identified mineral phases were: calcite, quartz, attapulgite and montmorillonite. Minor amounts of gypsum and feldspar were also observed. Table (1) presents the chemical composition of the raw claystone sample. It is worth to note here, that the chemical composition of attapulgite and montmorillonite in the Digma Formation is sufficiently close and these clays can hardly be identified from each other by chemical analysis. However, according to the data shown in Table (1), the raw claystone sample displays a high content of impurities, especially calcite, which is reflected by the high amount of CaO in the sample. The presence of the carbonate as well as some gypsum reflects the high loss on ignition (L.O.I) value of the raw claystone.

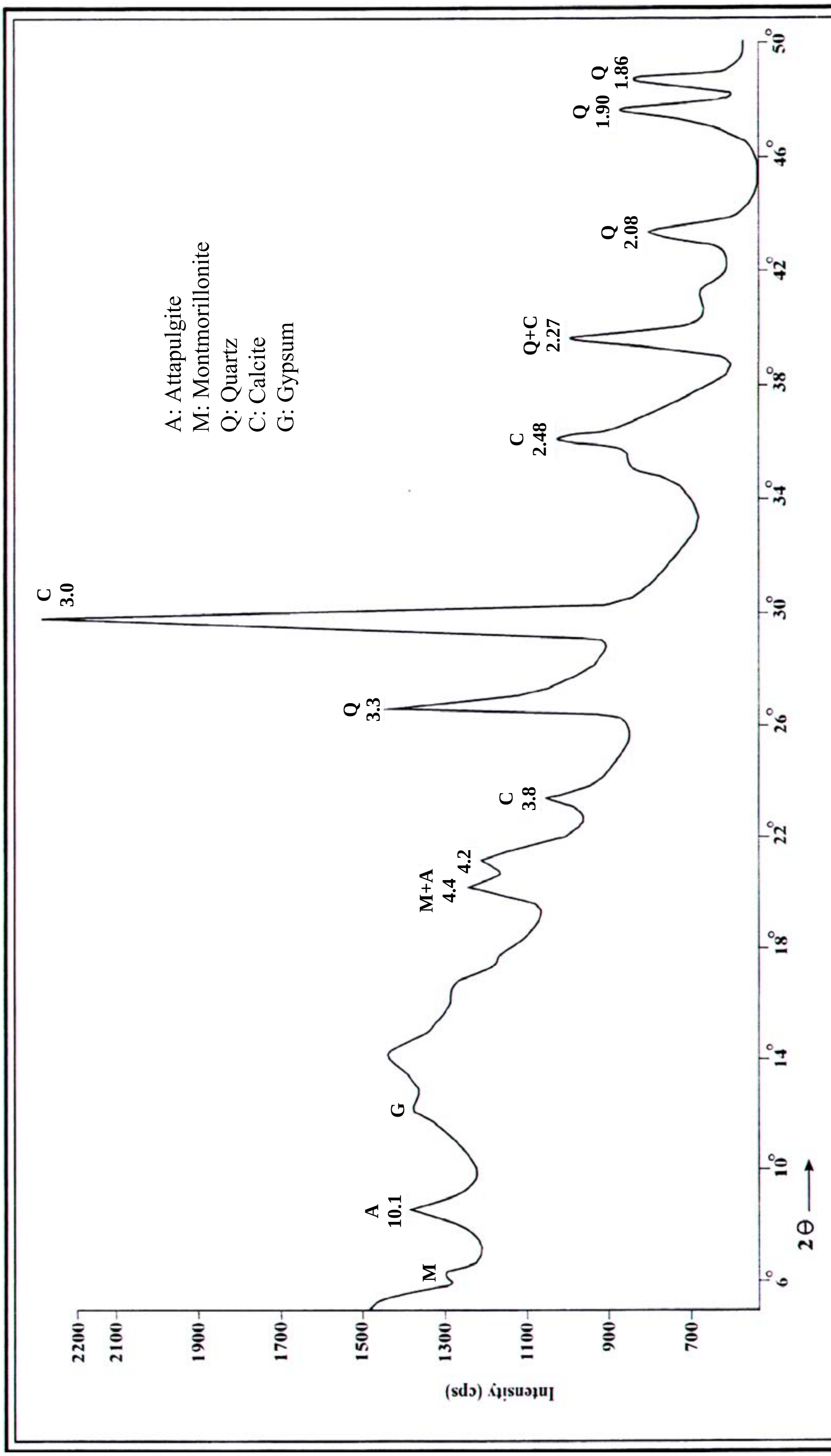

Fig.1: XRD – pattern of the raw claystone sample

- **Effect of Clay Concentration**

The resulting degritted raw claystone slurry (after removal of + 53 µm fraction) was about 13% solid concentration by weight, on dry basis. In this regard, the effect of clay concentration on the beneficiation of attapulgite from the raw claystone was investigated through the measurement of CaO content of the beneficiated clay at various solid concentrations. Tetrasodium pyrophosphate (TSPP) and sodium hexametaphosphate (SHMP) were employed as dispersant. The added amounts of dispersant to the claystone slurry were chosen of about 8% by weight of dry solid material of the slurry. The results are presented in (Fig.2) in the form of CaO percent versus solid concentration of raw claystone slurry. Based on visual observation, the claystone slurry exhibits a form of hydrogel suspension (i.e. the clay – water system possess high apparent viscosity) when dispersing with TSPP, at slurry concentration of 13% solid.

Analogous results were observed at slurry concentration of (13, 10, 7 and 5) % solid when SHMP was used as dispersing agent. This observation could be attributed to the transformation of Ca-montmorillonite to Na-montmorillonite, due to the presence of Na^+ ion in the slurry from the addition of dispersant (Ca-montmorillonite + $Na^+ \rightarrow$ Na-montmorillonite). Also, it seems that the hexametaphosphate ions render the transformed montmorillonite surface more hydrophilic, than pyrophosphate ions upon their adsorption on the mineral surface, leading to a higher swelling capacity of the montmorillonite and thus higher aqueous viscosity of the raw claystone slurry.

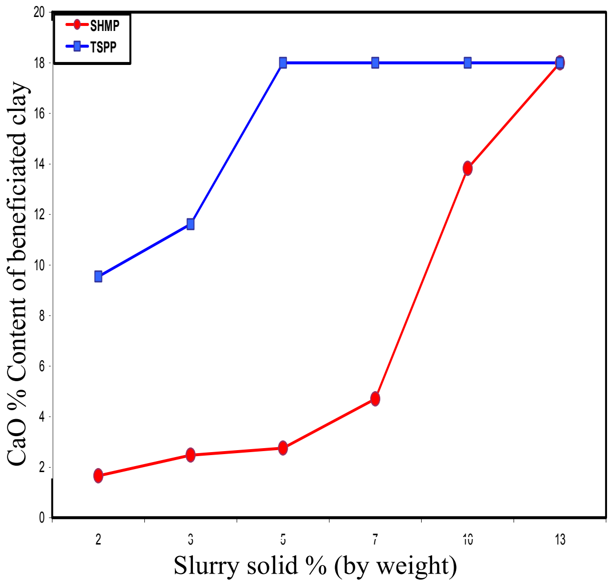

Fig.2: CaO contents of beneficiated clay as a function of solid slurry concentration

In such suspension, non-clay mineral particles are not free to settle down in accordance with their gravity and therefore, poor beneficiation of the clay occurred. As solid concentration decreased, the clay – water system becomes more fluid (low aqueous viscosity) and the free settling of non-clay gangue mineral particles were accordingly increased and separated from the clay minerals suspension.

As it can be seen from Fig. (2), that CaO content of the beneficiated clay decreases with the decrease of claystone slurry solid concentration indicating that the purity of the attapulgite – montmorillonite clay concentrates increases with decreasing claystone slurry solid concentration. Obviously, the degree of improvement in the beneficiation process was found much more (about 6 fold) for using TSPP more dispersant than that when using SHMP.

These results suggest that a good beneficiation of attapulgite – montmorillonite clay from the raw claystone could be achieved only with TSPP and at diluted claystone slurry of (2 – 5) % solid.

- **Effect of Dispersant Addition**

As observed from the results shown in Fig. (3), that the addition of about 8% (by weight) TSPP as dispersant indeed improves the beneficiation of the clay at a low concentration slurry (2 - 5% solid).

In order to save reagent consumption, the effectiveness of reducing dispersant addition on the beneficiation of clay minerals was studied at claystone slurry concentration of 5% solid. The results obtained are illustrated in Fig. (3) in term of CaO content of beneficiated clay versus TSPP addition. It can be seen from this figure that the CaO content of the beneficiated clay decreases with increase of dispersant addition to the level tested in this work (about 8% by weight). As the carbonate represents the major impurity present in the claystone deposit (Table 1), its reduction will accordingly enhance the purity of the beneficiated clay.

It is worth, however, to note that the dispersant requires producing an apparent low aqueous viscosity of attapulgite clay – water system that varies with deposits of different origins. It may also vary with different locations of the same deposit. In this respect, it was observed that the used dispersant quantity, in this work, was in sharp contrast to that carried out by Jacobs *et al*., (1971), for the processing of attapulgite of Georgia – Florida. The quantity of TSPP employed to attain low viscosity of attapulgite raw slurry was within the range of (1 – 3) % by weight of the claystone. The reason of employing high quantity of TSPP in practicing the beneficiation of attapulgite of Digma Formation could be attributed to the large amounts of montmorillonite that is associated with the deposit.

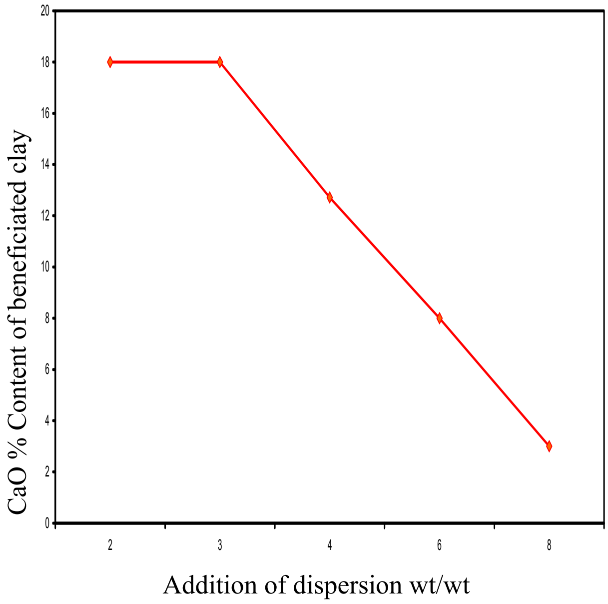

Fig.3: CaO content of beneficiated clay

It is well known that this clay mineral increases highly the aqueous viscosity of the clay – water system, particularly if it is of Na-type. Thus, large amount of dispersant is demanded to reduce the viscosity and fluidize the system. Fig. (4) shows the X-ray diffraction patterns of the claystone sample after being beneficiated by the dispersion and sedimentation processes. The chemical composition is shown in Table (2).

Table 2: Chemical analysis of the beneficiated attapulgite – montmorillonite claystone sample

SiO_2 %	Fe_2O_3 %	Al_2O_3 %	CaO %	MgO %	K_2O %	Na_2O %	SO_3 %	L.O.I %
51.5	5.32	16.09	3.86	5.5	0.47	0.83	<0.07	14

Comparing these results with those of the claystone before the beneficiation (Table 1 and Fig.1) it can be clearly seen that the quality of the beneficiated attapulgite – montmorillonite claystone is highly enhanced.

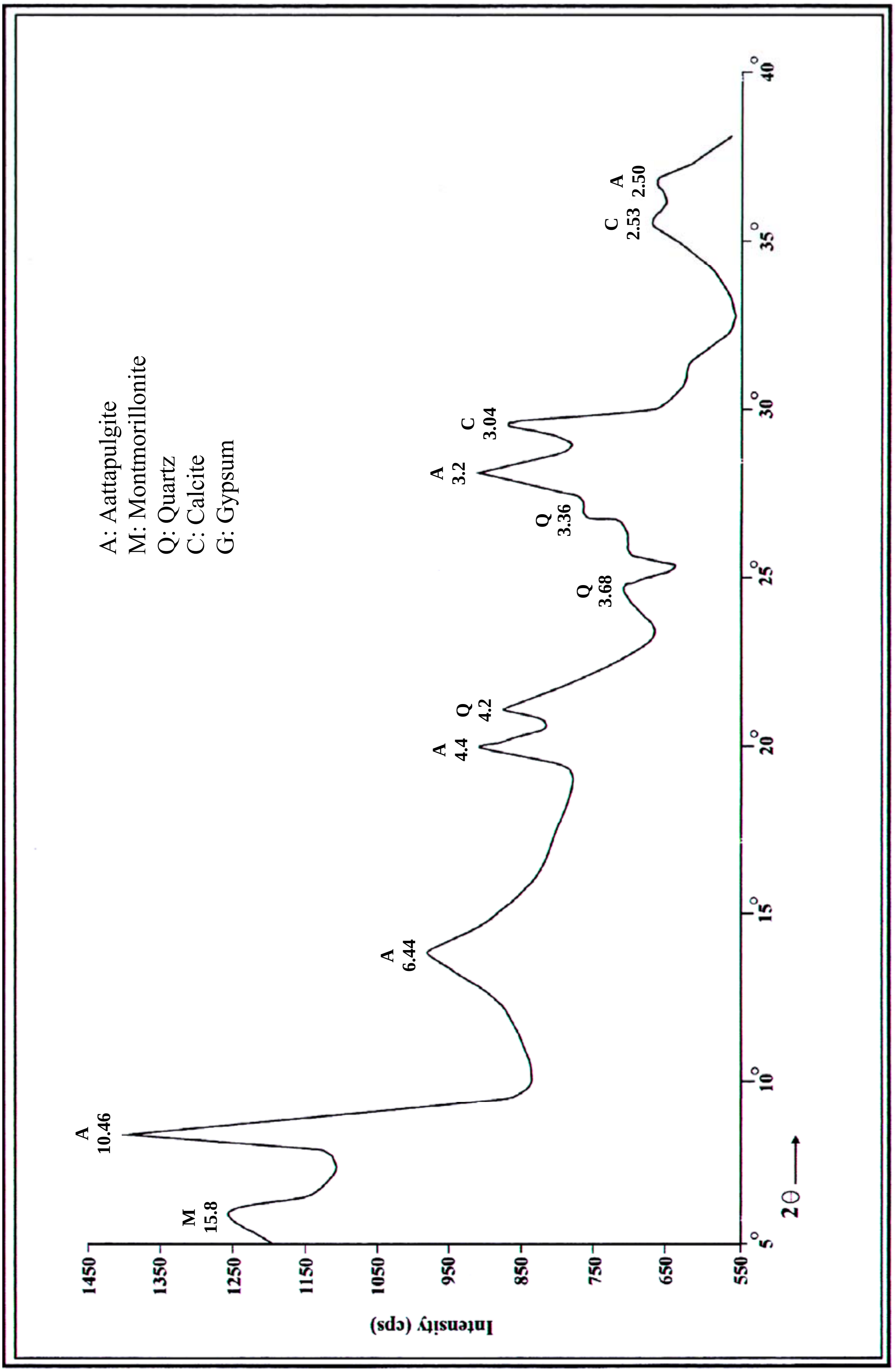

Fig.4: XRD – pattern of beneficiated clay

CONCLUSIONS

- The test results from the present work have shown that the dispersion sedimentation technique with tetrasodium pyrophosphate, as the dispersant, is very effective in beneficiating attapulgite-montmorillonite claystone from the crude claystone at a low slurry solid concentration.
- The dispersant quantity should be optimized in order to achieve good beneficiation results.
- It was found that tetrasodium pyrophosphate is much better than sodium hexametaphosphate, as a dispersant.

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