International Journal of Scientific Research and Sustainable Development (IJSRSD)

الاتحاد العربي للتنمية
المستدامة والبيئة

Physical and Chemical Assessment of Clay Raw Material for Industrial Use in the Sahabi Region, SE Libya

Abdelrhman H. Elmgariaf* and Saleh Emhanna

Department of Petroleum Engineering, Faculty of Engineering, University of Ajdabiya, Ajdabiya, Libya.

Article Information

Keywords:
Sahabi area; Clays; Industrial applications; X-ray fluorescence; Swelling test.

Corresponding author:
Abdelrhman H. Elmgariaf

E-mail:
abdelrhmanelmgariaf@gmail.com

Received: 12/6/2023
Accepted: 15/9/2023

Abstract

The As Sahabi region is located in northeast Libya at the southeastern margin of the Sirte Basin within a tectonic province called the Ajdabiya Trough. Most of this area, in the current climate, is a desert with Quaternary eolian dunes and sabkhas. This study's primary objective is to evaluate the Sahabi clay deposit's potential as an industrial resource by contrasting its chemical and physical characteristics with those of other standard clay types. In this study, the Sahabi clay was described using X-ray fluorescence (XRF) and swelling test methods on three samples collected from three different outcrops. The results of the XRF analysis showed very low percentages of silicon and aluminum, moderate to high percentages of impurities such as sulfur, magnesium, and iron in all samples, while the swelling test did not give any response in any of the three samples. Therefore, Sahabi clay is unsuitable for industry and drilling fluid.

التقييم الفيزيائي والكيميائي للمواد الخام الطينية للاستخدام الصناعي في منطقة الصحابي، جنوب شرق ليبيا

عبد الرحمن المقريف* و صالح امهنا

قسم هندسة النفط، كلية الهندسة، جامعة اجدابيا، اجدابيا، ليبيا

المستخلص

تقع منطقة الصحابي في شمال شرق ليبيا على الهامش الجنوبي الشرقي لحوض سرت داخل إقليم تكتوني يسمى حوض أجدابيا. معظم هذه المنطقة ، في المناخ الحالي ، عبارة عن صحراء بها كثبان وسبخات من العصر الرباعي. الهدف الأساسي لهذه الدراسة هو تقييم إمكانات رواسب الطين الصحابي كمورد صناعي من خلال مقارنة خصائصه الكيميائية والفيزيائية مع تلك الخاصة بأنواع الطين القياسية الأخرى. في هذه الدراسة ، تم وصف الطين الصحابي باستخدام طريقة فلورية الأشعة السينية (XRF) وطرق اختبار الانتفاخ على ثلاث عينات تم جمعها من ثلاث نتوءات مختلفة. أظهرت نتائج تحليل XRF نسبًا منخفضة جدًا من السيليكون والألمنيوم ، ونسبًا معتدلة إلى عالية من الشوائب مثل الكبريت والمغنيسيوم والحديد في جميع العينات ، بينما لم يعط اختبار الانتفاخ أي استجابة في أي من العينات الثلاث. لذلك فإن طين الصحابي غير مناسب للصناعة ووسائل الحفر.

معلومات عن البحث

الكلمات المفتاحية:

منطقة الصحابي؛ الطين؛ تطبيقات صناعية؛ فلورية الأشعة السينية ؛اختبار الانتفاخ

المؤلف المسؤول عن نشر البحث:

عبد الرحمن المقريف

الإيميل:

abdelrhmanelmgariaf@gmail.com

تاريخ الإرسال:

12/6/2023

تاريخ قبول النشر:

15/9/2023

1. INTRODUCTION

1.1. General

The definition of "clay" was formalized in 1546 by Agricola (Guggenheim & Martin, 1995). Clays and clay minerals are very important industrial minerals. Clay materials have been used in well over 100 recognized industrial applications. Clays are used in a variety of sectors, including those that process materials, agriculture, engineering, and building, as well as geology and environmental remediation (Murray, 2006). However, it has undergone several revisions since then, with most of the principles pertaining to plasticity, particle size, and fire hardening remaining the same (Ni, Lin, Wei, Yang, & Yang, 2013). Clay is an earth substance made mostly of small particles of hydrous aluminum silicates and other minerals. It is flexible while wet but becomes hard when fired (Rao, 2013). It is crystalline aluminum silicate that incorporates various impurities, according to its chemical makeup. Quartz flakes and, less frequently, zircon, apatite, granite, and other materials can be secondary components of clay (Saba et al., 2014). Iron hydroxides are common admixtures in clays. Clays may also include an organic material. small concentrations of greenish-colored manganese rock. There are four primary categories of clays based on their mineralogical composition: kaolinite ($Al_4(OH)_8Si_4O_{10}$), montmorillonite (complex hydrated silicates of Al, Mg and Na), illite (complex hydrated silicates of Al, Mg, Fe i Na) and haloizit ($Al_4(OH)_8Si_4O_{10}\times 4H_2O$) as well as around 30 different types of pure clays within these categories (Uddin, 2008).

According to geological investigations, there are two distinct forms of clay, depending on how they were deposited. Residual Clay is a category of clays that can be found where they originated. These kinds of clays are typically found in a very pure state and are deposited next to the igneous rocks from whence they originated. They are discovered to have a coarse particle size with a broad particle size dispersion based on their in-situ nature. These clays exhibit less flexibility as a result. A very pure form of residual clay with higher particle size and less flexibility is china clay. The other type is sedimentary clays, which are transported from their source by natural forces like water, wind, etc. and then deposited. Due to contaminants that are picked up during transmission and are preserved in the deposits, sedimentary clays are seldom found in their purest form. The sedimentary clay has a very high plasticity due to the very tiny particle sizes produced by the grinding action of clay particles in water, wind, and ice. Sedimentary clays like ball clay have finer particle sizes and excellent plasticity while not being very pure (Mousharraf, Hossain, & Islam, 2011).

This paper focuses on the economic evaluation of clay deposits in the Sahabi area. Although the beds of the clay cover a large area of the Sahabi area, it lacks precious metals, due to the absence of Magmatic and Hydrothermal deposits. The clay deposits in the study area considered to have secondary clay, In this study, we discuss the chemical composition of clay in the Sahabi area and how to use it in industry.

No study mentioned the possibility of using Sahabi clay in the industry. Most of the previous work in the Sahabi area focused on sedimentological and paleontological studies; only a few studies mentioned the deposits in the area, such as: (De Heinzelin & El-Arnauti, 1987) discussed the type of clay in the Sahabi Formation. (Beyer, 2008) studied the sedimentary sequence, which was dated using K-Ar dating and palaeomagnetism. (Muftah & El Ebaidi, 2012) discussed the geochemical and mineralogical analyses of the Sahabi clays from the Upper Neogene. The As Sahabi Formation's depositional environment was examined by (Muftah et al., 2013), and the results indicate to highly mature and reprocessed sediments of continental origin and felsic sources without any basaltic contribution. This study's primary objective is to evaluate the Sahabi clay deposit's potential as an industrial resource by contrasting its chemical and physical characteristics with those of other standard clay types.

1.2. Location of the study area

The As Sahabi region is located in northeast Libya at the southeastern margin of the Sirte Basin within a tectonic province called the Ajdabiya Trough, covering an area of about 375 km2. Most of this area, in the current climate, is a desert with Quaternary eolian dunes and sabkhas. The As Sahabi is an old Roman, Byzantine and Turkish fort, nowruined, situated 75 km south of Ajdabiya on the road to Jalu (Fig. 1).

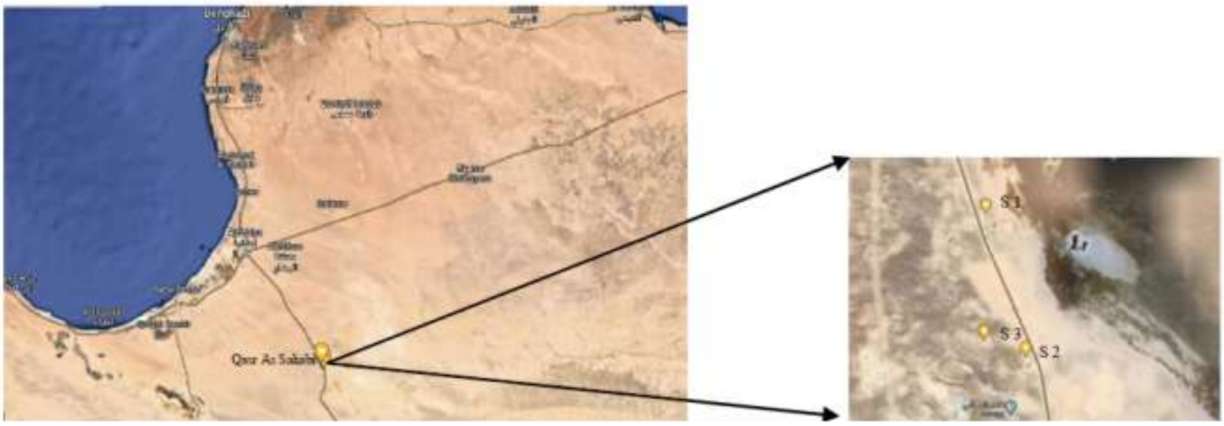

Fig. 1. Location map of the studied areas.

1.3. Geological setting

The Sirt Basin, which has a NW-SE trending pattern and covers an area of about 300.000 km^2, is the biggest and youngest sedimentary basin in Libya **(Fig. 2)**. It is surrounded by the Mediterranean Sea to the north, the Hun Graben to the west, a major dip-slip fault including the Antelat uplift dividing the basin from the Cyrenaica platform to the east, and the major Tibisti Sirt uplift to the south. **(Fig. 2)**. In the Cenomanian, the Sirt Basin was created, and a number of grabens and horsts with a NW-SE trend also developed. The Ajdabya trough, which contains the As Sahabi region, is one of the deepest portions of the basin (troughs), is considered as the eastern graben of the horst - graben system of Sirt Basin complex (El-Arnauti and El Sogher, 2004).

The Sirt arm is dominated by normal faults, which produce a series of sub-parallel horsts and grabens that form eastward-tilted fault blocks parallel to the structural axis. In addition to these characteristics, the structural strike of the Sarir arm is paralleled by E-W trending dextral shear zones. (Finetti, 1982).

According to (Morley et al., 1990), the southern and south-eastern portions of the Sirt basin are dominated by E-W and ESE-WNW trending faults, whereas the northwest portion of the Sirt basin is dominated by NW-SE trending dip-slip normal fault zones. Rift infill consists of basal continental marine siliciclastics of Triassic, Late Jurassic and Early Cretaceous age, fine-grained marine siliciclastics of late Cretaceous age, marine carbonates and evaporites of Late Cretaceous, Palaeocene, and Eocene age, and mixed carbonate-siliciclastics, of Oligocene, Miocene, and Plio-Pleistocene age. Continental siliciclastics from the Pleistocene and Holocene serve as the sequence's capstone.

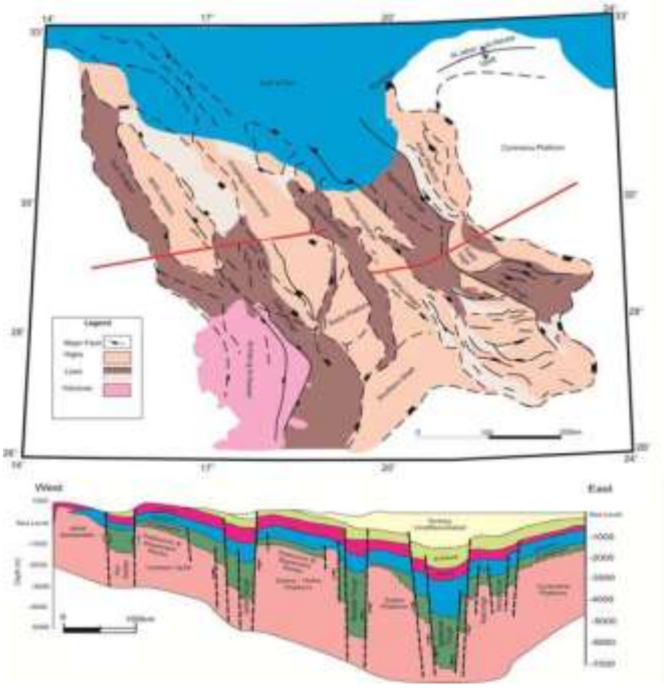

Fig. 2. The tectonic map shows a geological cross section of the Sirt Basin and the Ajdabya Trough. (Roohi, 1996)

2. MATERIALS AND METHODS

The steps of this study are:

1.Field work: In this step three samples have been collected from three different outcrops.
2.. Laboratory work: In the second step the work are as follows: -
Chemical analysis was carried out using X-ray fluorescence (XRF) by Libyan Cement Company Inc. (LCC), benghazi laboratory. -
Swelling Test was done by Jowfe Company for Oil Technology.

2.1. X-ray fluorescence(XRF)

An elemental analysis technique that provides quantitative chemical data is X-ray fluorescence (XRF). To differentiate between X-rays released from the sample surface, XRF uses an analytical crystal. An analytical crystal with a known composition has set interplanar spacing between its atoms' planes, which makes it easier to distinguish between different X-rays coming from a sample. **(Fig.3)** shows a typical XRF detection system in schematic form (Nasrazadani & Hassani, 2016)

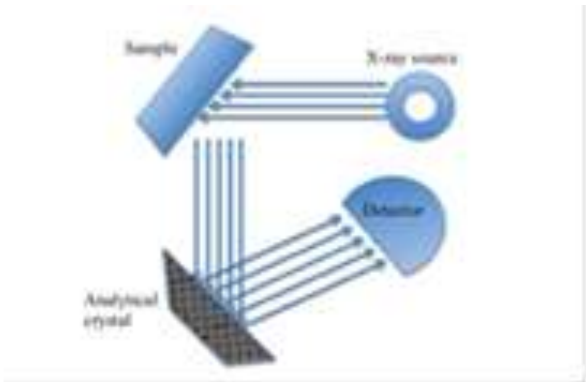

Fig. 3. X-ray detection system schematic diagram for the XRF technique.

To find compositional variation, several investigations on clays from various regions of the country have been carried out. Typically, such analysis is conducted using X-ray fluorescence (XRF). The XRF analyses in the research region are listed in Table 1:

Table 1. Chemical analysis data XRF (major oxides in wt. %) of the Sahabi deposits.

wt. % Major Oxides	Sample number			
	S1	S2	S3	Average composition
SiO_2	42.775 %	41.198 %	50.485 %	44.819 %
TiO_2	1.662 %	1.359 %	1.542 %	1.521 %
Al_2O_3	12.582 %	12.185 %	9.425 %	11.397 %
Fe_2O_3	4.329 %	6.190 %	5.411 %	5.310 %
P_2O_5	0.040 %	0.067 %	0.044 %	0.050 %
MnO	0.031 %	0.035 %	0.042 %	0.036 %
MgO	4.970 %	3.892 %	3.859 %	4.240 %
CaO	0.000 %	0.857 %	0.000 %	0.285 %
K_2O	1.598 %	1.901 %	2.282 %	1.927 %
SO_3	0.339 %	2.037 %	0.121 %	0.832 %
Cl	3.439 %	1.685 %	1.210 %	2.111 %
Na_2O	-	-	-	-
Sum	71.96 %	71.49 %	74.50 %	72.65 %

2.2. Swelling Test

Water molecules in clay minerals often adsorb on their exterior surfaces, mostly in broken bonds or in their interlayer gaps, connected to the interlayer cations or internal surface. With increasing water activity, the following modes of clay mineral hydration are distinguished (Güven, 1992): (i) interlamellar hydration via adsorption of limited amounts of water molecules on the internal surfaces of clay mineral particles; (ii) continuous hydration via unlimited adsorption of water on the internal and external surfaces of clay mineral particles; and (iii) capillary condensation of free water molecules in the inter-aggregate and intra aggregate micropores. Intercalation of 0–4 discrete layers of water molecules between individual 2:1 layers causes interlamellar or crystalline swelling due to interlamellar hydration, which mostly affects smectites and vermiculites. (Laird, 2006).

The swelling index was determined using the method of (Inglethorpe et al., 1993)., modified from (George Christidis, 1992). The CEC, which is a clear indication of the clay quality. The samples were activated with 1, 2, 3, 4, 5 and 6% Na_2CO_3 . The optimum concentration of Na_2CO_3 was determined to be the quantity that caused the greatest swelling in bentonites, and this concentration served as a guide for the following testing. The swelling volume provides an indirect indication of the bentonite grade (G Christidis & Scott, 1993); Inglethorpe et al., 1993). The Sahabi clay samples were dried, crushed and passed through a 125 um sieve and mixed it with an amount of Na_2CO_3 (sodium carbonate) between 1 to 6 %. A excellent bentonite will swell to a volume of around 25 mL, whereas a moderately swelling bentonite would swell to a volume of 15-20 mL. A top grade will expand to 30 mL or more (Inglethorpe et al., 1993).

The samples did not give any change with swelling. The comparison of the Sahabi clay's results to other standards for clay is shown in Table 2.

Table 2. Swelling test values for three Sahabi clay samples compared to Wyoming clay.

Type		Before 24 hrs.	After 24 hrs.	Swelling volume (ml)
Standard Composition	Wyoming (USA)	2.50	4.00	15
Locally Available Clay	S1 (Sahabi formation)	3.50	3.50	Nil
	S2 (Sahabi formation)	3.50	3.50	Nil
	S3 (Sahabi formation)	3.50	3.50	Nil

3. RESULTS

Clay material has many applications in different fields, these applications depend on the quality of the clay which may include: mineral composition, content of Al_2O_3 and SiO_2, impurity content, chemical stability, swelling, Place and value and whiteness. The raw clay from the Sahabi region was not tested for use in any production. Thus, from an academic and technological standpoint, investigating the suitability of this clay for any manufacturing is of interest.

3.1. Clay Bricks Manufacturing.

Bricks are small rectangular construction materials that are often used to make walls. Ancient Greeks and Romans used bricks to construct their houses because it was an inexpensive and available material.
(Punmia, Jain, & Jain, 2003) the constituents of a good brick earth are:
Silica (sand) – 50% to 60% by weight
Alumina (clay) – 20% to 30% by weight
Lime – 2 to 5% by weight
Iron oxide – ≤ 7% by weight
Magnesia – less than 1% by weight

Comparing the ideal composition of the bricks with the results of analyzing the Sahabi clay samples, the results showed that the use of Sahabi clay is not appropriate in the manufacture of bricks.

3.2 Manufacture of Portland Cement

The process of making Portland cement involves heating raw materials including oxides of calcium, silicon, and aluminum to temperatures close to 1500°C, followed by grinding the resultant material with a little quantity of gypsum.

The composition of standard cement and its comparison to Sahabi clay are shown in the following table:

Table 3. XRF analysis of Sahabi and ASTM C150 clay

Composition (%)	Locally Available Clay	Standard Composition *ASTM C150	
	S1+S2+S3(Sahabi formation) Average composition	Portland cement	Raw clay
SiO_2	44.819 %	20.49 %	59.7 %
Al_2O_3	11.397 %	4.26 %	25.53 %
Fe_2O_3	5.310 %	3.14 %	5.22 %
CaO	0.285 %	63.48 %	0.16 %
MgO	4.240 %	2.11 %	1.37 %
SO_3	0.832 %	2.9 %	0.07 %
Na2O+ K2O	1.927 %	0.49 %	2.41 %

*ASTM C150: American Society of Testing Materials ASTM C150 2016 ASTM Int.

3.3. Ceramic industry

Clay is one of the main raw materials used in the traditional ceramic industry. Although we did not do a complete analysis of the clay material in the Sahabi area to evaluate its use in the ceramic industry, because ceramic requires several tests, including: physical property, dry shrinkage, firing shrinkage, dry flexural strength, thermal flexure, specific surface area and water absorption. However, based on the results obtained from the chemical analysis, we give a first impression of the possibility of using Sahabi clay in the ceramic industry. The chemical analysis Table 4 shows that the oxides in the clay of the Sahabi formation compared to Turkish standard TS EN 14411 (2006), (Celik, 2010).

Table. 4 comparison between Locally available clay and Standard Composition

Composition (%)	Locally Available Clay	Standard Composition
	S1+S2+S3(Sahabi formation) Average composition	Istanbul clay (IC)
SiO_2	44.819 %	55.85
Al_2O_3	11.397 %	26.46
Fe_2O_3	5.310 %	3.23
TiO_2	1.521 %	1.21
CaO	0.285 %	0.34
MgO	4.240 %	0.58
Na_2O	-	0.11
K_2O	1.927 %	2.00
SO_3	0.832 %	0.22
P_2O_5	0.050 %	0.12

4. DISCUSSION

Because of its low chemical content in silica and aluminum and high impurity levels, Sahabi clay cannot be used to make bricks, cement, ceramics, or drilling fluid. Based on the XRF analysis, clay samples from the Sahabi formation It is not suitable for use in the manufacture of bricks because the percentage of aluminum in all samples is less than 20%. Furthermore, XRF analysis in Table 3, a comparison of clay samples from the Sahabi Formation with standard compositions, reveals that the standard material contains significantly more SiO_2 and Al_2O_3. In addition, most Sahabi clay types also have high levels of impurities such as MgO and SO_3. As a result, Sahabi clay is not considered suitable for use in the cement industry. Also, Sahabi clay cannot be used in the ceramic industry because of its low SiO_2 and Al_2O_3 content, where the aluminum content in the ceramic is over 20%, as well as the presence of high levels of impurities such as Fe_2O_3 that could reduce the brightness of the ceramic. Finally, clay minerals play an important role in drilling hydrocarbon reservoirs because of their direct effects on the production process. Based on the results of the swelling test in Table 2, both unprocessed clay and clay that had been handled with up to 6% Na_2CO_3 did not swell to the same extent as standard bentonite, so it is not suitable to use Sahabi mud in the drilling fluid.

5. CONCLUSION

The Clay in the Sahabi area is considered to have a secondary clay. Although the clay covers a large area of Sahabi Formation , it is considered to be of poor quality due to the absence of Magmatic deposits. Analysis of major oxides was done by X-ray fluorescence (XRF) technique, Where the results showed that it is not possible to use Sahabi clay in the manufacture of bricks, cement and ceramics, due to the low chemical content such as silica and aluminum, in addition to the large amount of impurities. Also Both unprocessed clay and clay that had been treated with up to 6% Na_2CO_3 did not swell to the same extent as standard bentonite.

ACKNOWLEDGEMENT

The authors extend their thanks to the Cement Factory and Al-Jouf Company for their assistance in analyzing the samples.

6. REFERENCES

Beyer, C. (2008). Establishment of a chronostratigraphical framework for the As Sahabi sequence in northeast Libya. *Garyounis Scientific Bulletin, 5*, 59-69.

Celik, H. (2010). Technological characterization and industrial application of two Turkish clays for the ceramic industry. *Applied clay science, 50*(2), 245-254.

Christidis, G. (1992). *Origin Physical and Chemical Properties, of the Bentonite Deposits from the Aegean Islands of Milos, Kimolos, and Chios, Greece.* University of Leicester,

Christidis, G., & Scott, P. (1993). Laboratory evaluation of bentonites. *Industrial Minerals*(311), 51-57.

De Heinzelin, J., & El-Arnauti, A. (1987). The Sahabi Formation and related deposits. *Neogene Paleontology and Geology of Sahabi. Alan R. Liss, New York, 121*.

El-Arnauti, A. and El Sogher, A. (2004) Short Notes and Guidebook on the Geology of Qasr As Sahabi Area. Tripoli, Earth Science Society of Libya, pp. 1-95.

Finetti, I. (1982). Structure, stratigraphy and evolution of central Mediterranea. *Bollettino di Geofisica Teorica ed Applicata*, *24*(96), 247-315.

Guggenheim, S., & Martin, R. (1995). Definition of clay and clay mineral: joint report of the AIPEA nomenclature and CMS nomenclature committees. *Clays and clay minerals, 43,* 255-256.

Güven, N. (1992). Molecular aspects of clay-water interactions.

Inglethorpe, S.D.J., Morgan, D.J., Highley, D.E., Bloodworth, A.D., 1993. Industrial minerals lab-oratory manual: bentonite. British Geological Survey Technical Report, WG/93/20.

Laird, D. A. (2006). Influence of layer charge on swelling of smectites. *Applied clay science, 34*(1-4), 74-87.

Morley, C.K., Nelson, R.A., Patton, T.L., Munn, S.G., 1990. Transfer zones in the East African rift system and their relevance to hydrocarbon exploration in rifts. AAPG bulletin, 74, 1234-1253.

Mousharraf, A., Hossain, M. S., & Islam, M. F. (2011). Potential of locally available clay as raw material for traditional-ceramic manufacturing industries. *Journal of Chemical Engineering, 26*, 34-37.

Muftah, A., & El Ebaidi, S. (2012). *Mineralogical and geochemical investigations of the Upper Neogene Sahabi clays in As Sahabi area–Northeast Sirt Basin. In.* Paper presented at the The 11th Mediterranean Petroleum conference and Exhibition, Tripoli, Libya.

Muftah, A. M., Pavlakis, P., Godelitsas, A., Gamaletsos, P., & Boaz, N. (2013). Paleogeography of the Eosahabi River in Libya: New insights into the mineralogy, geochemistry and paleontology of Member U1 of the Sahabi Formation, northeastern Libya. Journal of African Earth Sciences, 78, 86-96.

Murray, H. H. (2006). *Applied clay mineralogy: occurrences, processing and applications of kaolins, bentonites, palygorskitesepiolite, and common clays*: Elsevier.

Nasrazadani, S., & Hassani, S. (2016). Modern analytical techniques in failure analysis of aerospace, chemical, and oil and gas industries. *Handbook of Materials Failure Analysis with Case Studies from the Oil and Gas Industry*, 39-54.

Ni, J., Lin, J., Wei, R., Yang, H., & Yang, Y. (2013). Does the distribution of polycyclic aromatic hydrocarbons in soil particle-size separates affect their dissipation during phytoremediation of contaminated soils? In *Functions of natural organic matter in changing environment* (pp. 669-672): Springer.

Punmia, B., Jain, A. K., & Jain, A. K. (2003). *Basic civil engineering*: Firewall Media.

Roohi, M. (1996). A geological view of source-reservoir relationships in the western Sirt Basin. *Geology of the Sirt Basin: Amsterdam, Elsevier, 2,* 323-336.

RAO, K. S. (2013). Strategic use of soil in war operations: the role of dispersion flocculation thixtrophy and plasticity of clay. Defence Sci. J., 1(2), 192-204.

Saba, S., Delage, P., Lenoir, N., Cui, Y. J., Tang, A. M., & Barnichon, J.-D. (2014). Further insight into the microstructure of compacted bentonite–sand mixture. *Engineering geology, 168,* 141-148.

Uddin, F. (2008). Clays, nanoclays, and montmorillonite minerals. *Metallurgical and Materials Transactions A, 39*(12), 2804-2814.