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Effect of Clay Adsorption on the Petroleum Refining Industry

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Abstract

In this work, ceramic crude petroleum filter was prepared from low-cost materials based on Kaolin powder and Alumina, with combustible materials as palm fronds powder which acts as pore creating the agent. The filter samples with different content (5,10,15,25,35 and 45) % of palm fronds were fabricated using a dry pressing method and fired at1100 ˚C. After that, samples of porous ceramic filters were prepared and some tests were carried out, such as characterization by X-ray diffraction, physical properties (linear shrinkage, mass loss) and mechanical properties (compressive strength and diametrical strength). Results showed that linear shrinkage was 7.7%, loss in mass was 49.4%, compressive strength was 2.2 Mpa and diametrical strength was 1.7 Mpa with a 45% ratio of fine (P.F). Crude petroleum passing through the filters evaluated by tests, such as (API Gravity, Sulfur Content and Asphaltenes Content). The result of API Gravity before immersion crude petroleum filter balls was 24.70 and after immersion crude petroleum filter balls for 14 days for 30% (P.F) increased to 32.5. Sulfur Content before immersion crude petroleum filter balls was 3.76 and after immersion crude petroleum filter balls for 14 days for 30% (P.F) decreased to 2.6.So Asphaltenes Content before immersion crude petroleum filter balls was 6.68 and after immersion crude petroleum filter balls for 14 days for 30% (P.F) decreased to 1.6.

Keywords: Crude Petroleum, Ceramic Filter, Natural additive, Alumina, Vanadium, nickel, asphaltenes, sulfur.

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تأثير امتزاز الطين على صناعة تكريرالنفط الخام

ايناس محي هادي وخلود حليم يوسف

قسم العلوم التطبيقية - الجامعة التكنولوجية

الخلاصة

في هذا العمل ,تم تحضير فلترالنفط الخام السيراميكي من مواد منخفضة التكلفة تعتمد على مسحوق الكاولين والألومينا مع مواد قابلة للاحراق مثل مسحوق سعف النخيل الذي يعمل على خلق المسامات. عينات الفلتر بمحتوى مختلف (5، 10، 15، 25، 35 و 45) % بالوزن من سعف النخيل ثم شكلت العينات باستخدام طريقة الكبس الجاف وحرقت عند 1100 درجة مئوية. بعد ذلك، تم تحضير عينات الفلترالسيراميكي المسامي ، وتم تقييم بعض الاختبارات التركيبية مثل حيود الأشعة السينية، والخصائص الفيزيائية (التقلص الطولي و الفقدان بالكتلة) والخصائص الميكانيكية (متانة الانضغاط ومتانة الكسر المحوري). أظهرت نتائج التقلص الطولي 7.7٪، والفقدان بالكتلة 49.4 ٪، ومتانة الانضغاط 2.2 Mpa، ومتانة الكسر المحوري 1.7 Mpa عند نسبة 45٪ من (P.F) الناعم. تم تقييم النفط الخام الذي يمر عبر الفلاتر بواسطة اختبارات مثل (الكثافة النوعية حسب معهد النفط الأمريكي API، ومحتوى الكبريت ومحتوى الاسفلتين) وكانت نتيجة API قبل غمر كرات تصفية النفط الخام 24.70 وبعد غمر كرات تصفية النفط الخام لمدة 14 يومًا مع (PF) الناعم عند نسبة 30٪ تزداد إلى 32.5، محتوى الكبريت قبل غمر كرات تصفية النفط الخام كان 3.76 وبعد غمر كرات تصفية البترول الخام لمدة 14 يومًا مع (PF) الناعم عند نسبة 30٪ تنخفض إلى 2.6. حتى محتوى الأسفلت قبل غمر كرات تصفية النفط الخام كانت 6.68 وبعد غمر كرات تصفية النفط الخام لمدة 14 يومًا مع (PF) الناعم عند نسبة 30٪ تنخفض إلى 1.6.

كلمات مفتاحية : النفط الخام، فلتر السيراميك، المضافات الطبيعية، الألومينا، الفاناديوم، النيكل، الإسفلت، الكبريت.

Introduction

Various types of ceramic materials have been used as filter generally and especially with Petroleum. The main type of ceramics currently in use for the manufacturing of filtration membranes consists of oxides: alumina, zirconia or Titania [1].

Recently, due to the wide application of various materials involving metals, ceramics, polymers, composite materials, semiconductors, and biomaterials, porous ceramics have become increasingly important in industry [2]. Porosity affects the properties, characteristics, strength (bending and compression) and density of the material. Production of porous materials has a long history. Mainly used for structural applications of concrete, cement, brick and refractory materials. Porous ceramics are commonly used in diesel exhaust filters, catalytic carriers and industrial hot gas filters [3].

Adsorption process is one of the simplest and efficient separation methods, as it can be achieved at ambient pressure, temperature and without use of any expensive materials. Adsorption process is used to treat crude oil [4].

Crude petroleum especially from Al-Ahdab well in the province of Kut has a big problem resulted from its low percentage of API Gravity, high percentage of sulfur content, and metallic Content. Thus, it has been classified as a heavy crude petroleum well which is considered undesirable by the importing companies.

Therefore, the purpose of this study is to obtain light crude petroleum by removing or reducing these components, and obtain the results that are nearest to the required specifications. The filter is environmentally friendly, harmless, Cheap price and inexpensive.

Materials and Methods

Samples Preparation

Kaolin sample was collected from the western desert (Dwekhla) in Iraq. Use a ball mill to grind the clay so that the particle size is less than or equal to 75 µm. The composition of kaolin powder was determined using wet chemical analysis technique by (XRF) is a well-established and powerful tool for nondestructive elemental analysis of any material as illustrated in Table1 obtained from the state Establishment of Geological Survey and mining of the ministry of industry and minerals.

Palm fronds powder that was used as a pore former was obtained from palm fronds.
It was dried in the sun, then ground and sieved to obtain material particles sizes with a diameter ≤ 0.3 ≥ 400 µm, as illustrated in table 2. Sieved Kaolin powder ≤ 75 µm and combustible material as Palm fronds (P.F.) were mixed in the selected proportion as illustrated in table 3.

Table 1: Kaolin chemical analysis by (XRF)

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O	Na_2O	MgO	L.O.I
Kaolin wt. %	49.38	32.72	2.07	1.19	1.08	0.44	0.22	0.18	12.42

Table 2: Particle size of Materials

Particle size	Kaolin	Al_2O_3	Palm fronds (P.F.) (Fine)	Palm fronds (P.F.) (Medium)	Palm fronds (P.F.) (Coarse)
µm	≤ 75	≤ 37	≤ 0.3	0.3≤ P.F ≥125	125≤ P.F≥400

Table 3: Compositions of Prepared Filter Specimens

Mixture (Kaolin70%&alumina 30%)	P.F.%
100	0
95	5
90	10
85	15
75	25
65	35
55	45

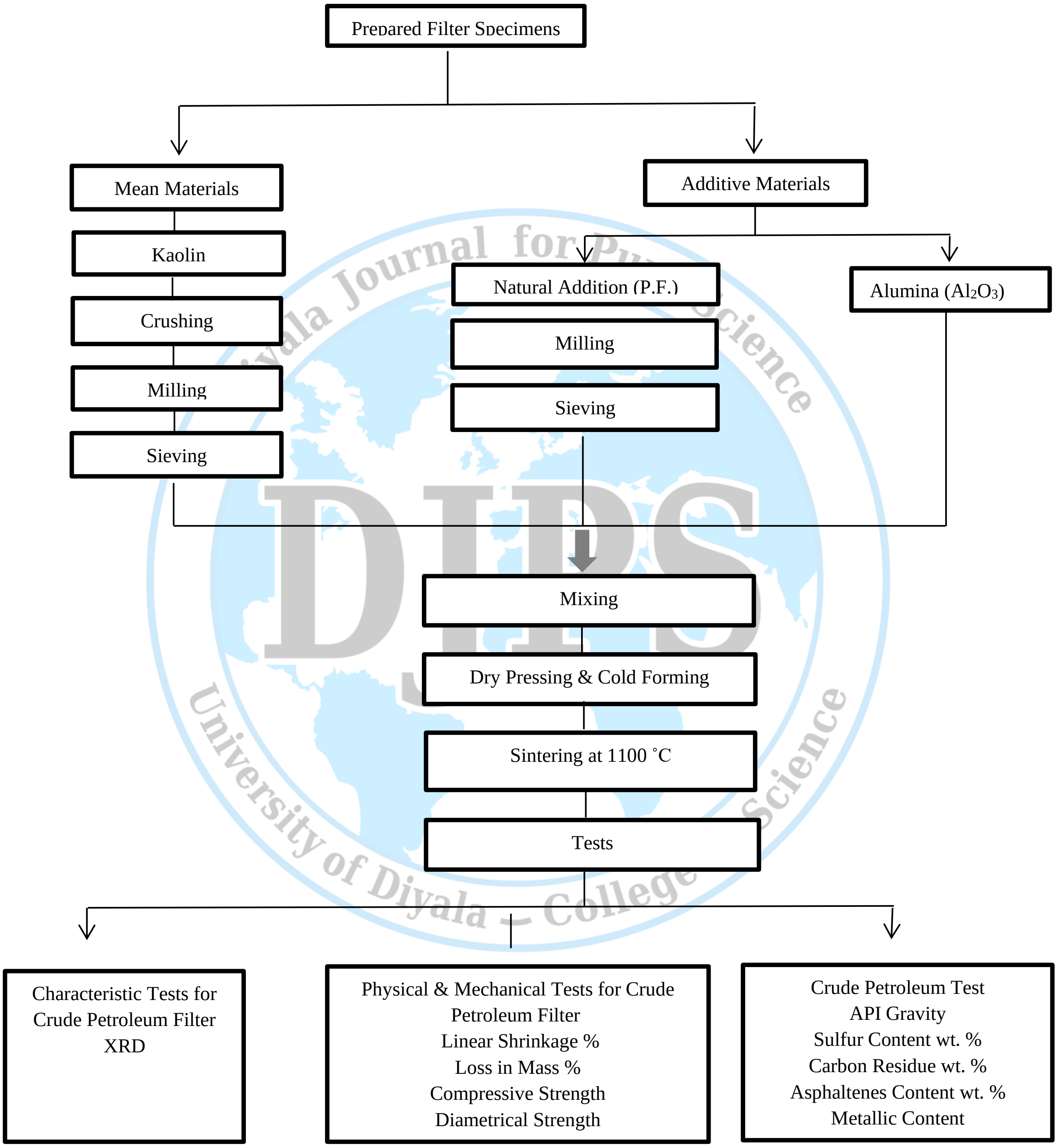


Figure 1: Scheme work preparation of porous ceramics

Samples forming

Then, the mixture was molded into disk shapes (25 mm in diameter and 3 mm in thickness) at a pressure of 4 ton by dry pressing, as shown in the figure. 2. Balls specimens were prepared using the cold forming method show in the figure. 3. After forming, sinter the specimens (Disk and Ball) at 1100 (˚C) in several stages, as shown in table 4. Then balls with a weight ratio 30 % of (P.F) from fine particle size were immersed in Crude Petroleum for 14 days [5].

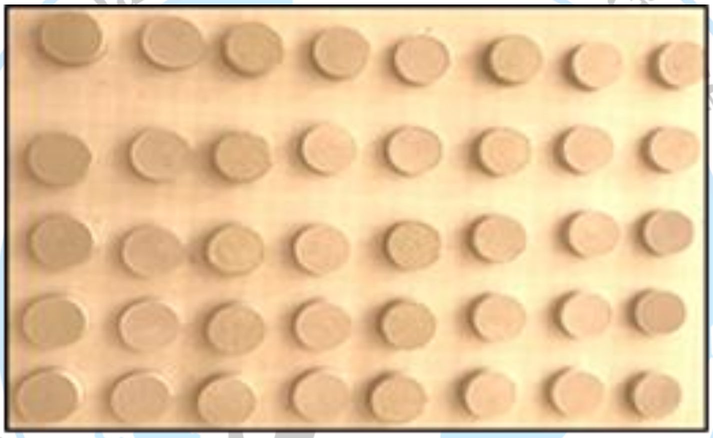


Figure 2: Porous ceramic Disk Specimens

Figure 3: Porous Ceramic Balls Specimens

Table 4: Stages of sintering

Stage	Temp.(°C)	Heating rate (°C/min)	Packing time (hr)
The First	(25 - 700)	5.62	2
Second	(700 - 900)	3.33	1
Third	(900-1100)	1.66	2

Testing:

Physical Tests for Crude Petroleum Filter:

- **Linear Shrinkage (L.SH.)**

The linear shrinkage of all specimens was determined by measuring the differences in disk diameters before and after sintering using a vernier.

According to (ASTM 326), (L.SH) as shown in equation:

$$L.SH. = \frac{Lo-L}{Lo} \times 100\% \quad (1)$$

L_o: The length of the sample before firing.

L: the length of the specimen after firing.

- **Loss in Mass (L.M):**

It is usually determined by using Vernier to measure the initial and final mass of specimens before and after the firing process.

(L.M.) is calculated by the following equation according to (ASTM C1407).

$$L.M. = \frac{Mo-M}{Mo} \times 100\% \quad (2)$$

M_o: the mass of the specimen before firing.

M: the mass of the specimen after firing.

Mechanical Tests for Crude Petroleum Filter:

- **Compressive Strength (C.S) Test:**

The compressive strength test was determined according to (ASTM C-773) by using cylindrical specimens. Compressive stress was calculated by the following equation:

$$\sigma = \frac{F}{A} \quad (3)$$

σ: Compressive strength (MPa)

F: Maximum applied load (N)

A: Cross section area of the specimens (mm^2)

- **Diametrical Strength (D.S) Test:**

The mechanical resistance test is performed by measuring the diametrical strength using a hydraulic piston. The specimen is placed vertically under the piston.

(D.S) was calculated by the following equations according to (ASTM C773).

$$\sigma_D = \frac{2F}{\pi dD} \quad (4)$$

σ_D: tensile strength splitting (MPa).

F: applied load (N).

D: specimen diameter (mm).

L: length of the specimens (mm).

Crude Petroleum Test:

Crude petroleum is very complex. Relatively simple analytical tests are conducted on crude oil and the correlation between these results and experience is used to evaluate crude oil used as a raw material in specific refineries.

More useful attributes are:

American Petroleum Institute (API) Gravity:

The density of oil in the United States is expressed in terms of API gravity rather than gravity. It is related to specific gravity in such a way that an increase in API gravity corresponds to a decrease in specific gravity.

The unit of API gravity is API, which can be calculated by the following specific gravity:

$$API = \frac{141.5}{specific\ gravity} - 131.5$$

Where:

Specific gravity: Under the standard, the ratio of the weight of oil per unit volume to the weight of water of the same volume.

Sulfur Content wt. %:

Sulfur content is expressed as a weight percentage of sulfur and varies from less than 0.1% to more than 5%. Crude oil with sulfur content greater than 0.5% generally requires more extensive processing than crude oil with lower sulfur content [6].

Carbon Residue wt. %:

In the absence of air, the residual coke is determined by distillation. The amount of carbon residue is roughly related to the content of asphalt in crude oil and the content of recoverable lubricating oil fractions. In most cases, the lower the carbon residue, the higher the value of crude oil. This is expressed by the percentage of carbon residue tested by Rams bottom carbon residue according to (ASTM D-524).

Asphaltenes Content wt. %:

It is the highest molecular weight and complex part of petroleum. Asphaltene content represents the amount of coke that can be expected during processing [7, 8]. The insoluble matter asphaltene content is separated and dried by filtration, can be determined by dual wavelength spectrophotometry According (ASTM D-3279).

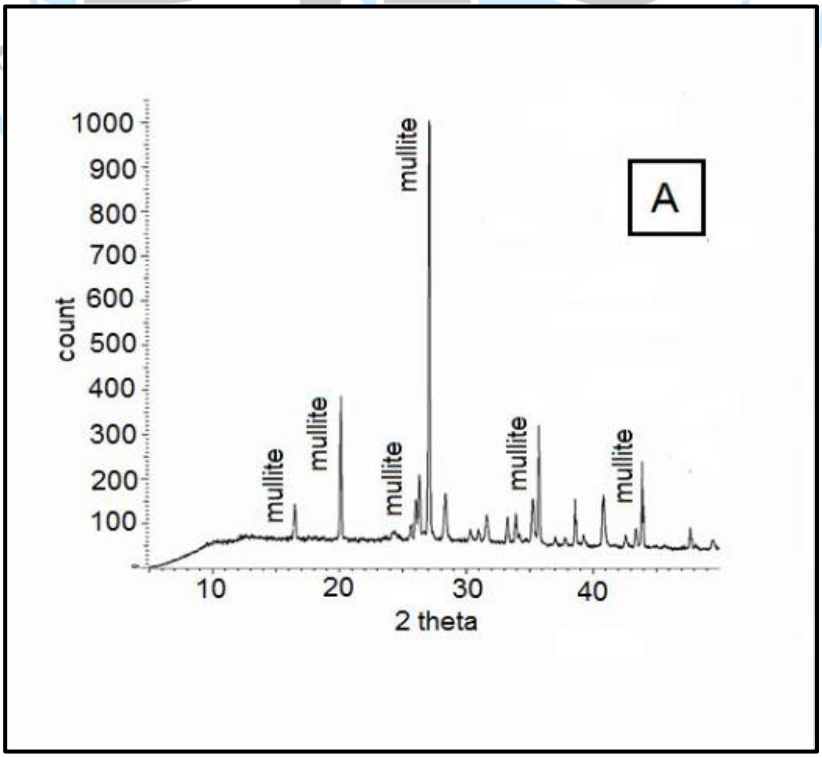
Metallic Content (Ni, V, and Fe):

The metal content in crude oil can vary from a few ppm to more than 1000 ppm [9]. They have several disadvantages such as; they affect activities of catalyst, corrosion, deterioration of refractory furnace lining, and stacks [10]. Metals are determined by Spectroil M which is a standard instrument to fuel analysis. According (ASTM D6728).

Results and Discussion

X-ray diffraction

By using X-ray diffraction analysis, the phases of the ceramic crude petroleum filter samples were studied, as shown in Figure 4. A and B After firing at 1100(°C).



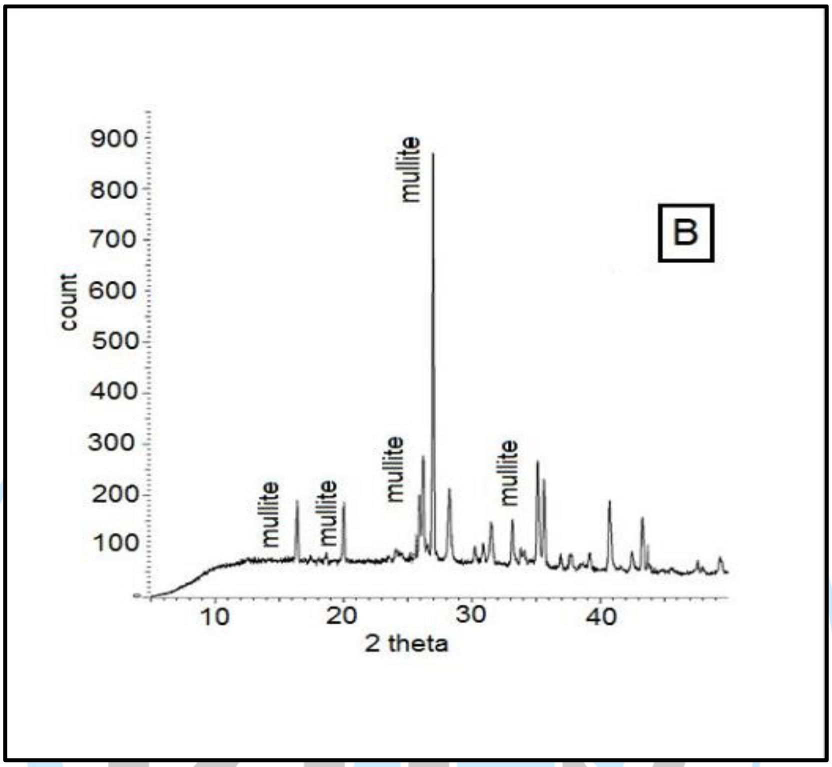


Figure 4: X-Ray diffraction analysis of ceramic crude petroleum filters. A: for 30% fine (P.F) filter. B: for 30% coarse (P.F) filter

According to the results of X- Ray diffraction analysis, we observe that mullite phase represents the mean ceramic phase and glass phase represents the binder phase in ceramic body after firing process. The mullite is phase shown as sharp peak, while the glass phase an shows an amorphous phase. In a raw material with a constant percentage between alumina (Al_2O_3) and silica (SiO_2) as the main component of clay, the mullite phase in the kaolin raw material starts to appear at a temperature higher than 1000 (˚C). The free amount of silica and flax (K_2O, Na_2O, Fe_2O_3, etc.) forms the liquid phase. The most important crystalline phase in many clay ceramic products is mullite.

It is a mineral in the form of ($3Al_2O_3.2SiO_2$) and has important properties (low thermal expansion, low thermal conductivity, biological inertness, very good chemical stability); so mullite phase suitable for crude petroleum filter application. That means ceramic crude petroleum filter can be successfully operated efficiently for a long time. From figure 4A we

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observe mullite intensity decreases with the increasing of (P.F) ratio since the raw materials kaolin decreases in other words materials that produce mullite phase decreases. The glass phase is found with little amount. From Fig. 4B, we observe that the intensity of the mullite phase decreases as the (P.F) ratio increases.

Linear Shrinkage (L.SH.):

The effect of size for addition particle (fine, medium, coarse) obtained the fine particle size has the least Linear Shrinkage than the (medium – coarse) particle size because the fine particle size has large surface area and the volume is smaller therefore taken large space within crude petroleum filter, when the adding is (medium – coarse) the glass phase high efficiency in filling the pores and pulls the crystals of the mullite because the generated pores are large therefore it capable in filling the pores with high efficiency to pulls the crystals of the mullite . As for the additional fine particle size (P.F≥300µm), it will produce very small pores of ≅ 300 µm. Therefore, due to its small size, the efficiency of the pores generated by the glass phase filling is reduced, so we have obtained higher pores rate.

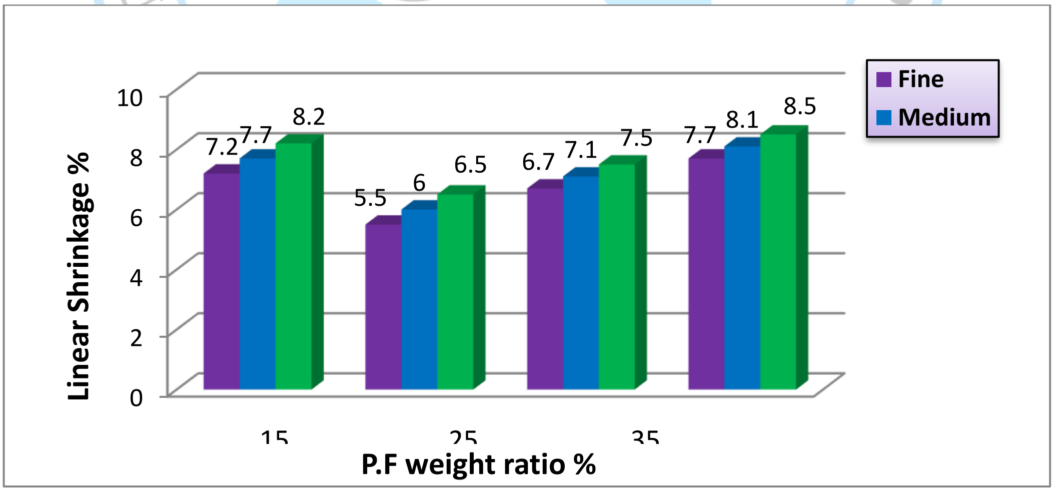

Figure 5: Effect of particle size on the linear shrinkage of crude petroleum filters with ratios (15, 25, 35, and 45%).

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Loss in Mass (L.M)

the effect of different size for addition particle, at the same addition of (P.F) ratio the fine particle has large surface area and less material mass so it taken large volume to reach same addition ratio compared with addition particle (medium –coarse) therefore the ceramic material volume decreases which generated ceramic phases with a high mass and it causes high loss in mass as a result burning addition material which taken large volume than the ceramic body.

When addition the fine particle (P.F) leads to higher pores ratio generation than addition particle (medium –coarse) because the fine particle (P.F) addition generated small pores does not fill easily with the glass phase therefore, the high ratio of porosity that means higher loss in mass compared with addition particle (medium –coarse) in which the pores are medium or large and fill easily with the glass phase so the porosity is lower, the loss in mass is lower.

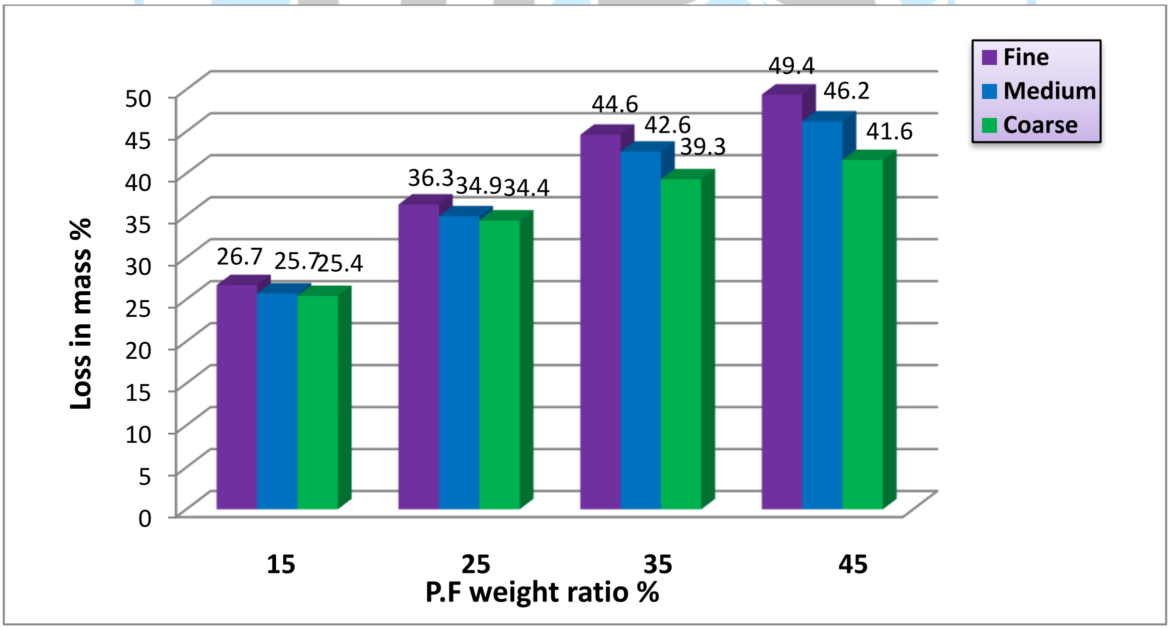

Figure 6: Effect of particle size on the loss in mass of crude petroleum filters with ratios (15, 25, 35, and 45) %.

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Compressive Strength (C.S)

The effect of particle size on the compressive strength of crude petroleum filter with ratios (15, 25, 35, and 45) % is shown in figure 7. It can be noted that the strength of specimens with coarse (P.F) is lower compared to the specimens with fine (P.F) because the last behavior were of poor bonding in the structure since it has a high apparent porosity ratio, which give high percentage of pores, and these specimens have the lowest compressive strength among all specimen.

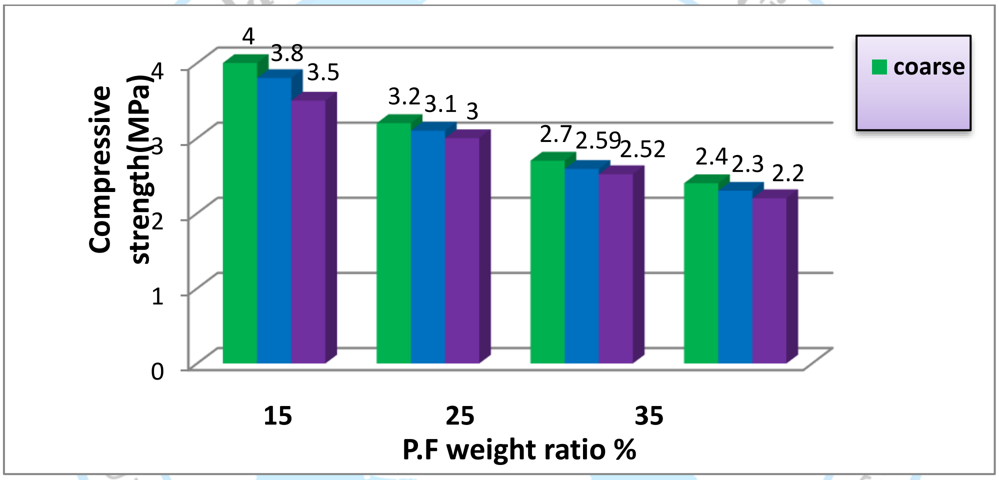

Figure 7: Effect of particle size on the compressive strength of crude petroleum filters with ratios (15, 25, 35, and 45) %.

Diametrical Strength (D.S)

The effect of particle size on the diametrical strength of crude petroleum filters with ratios (15, 25, 35, and 45) % is presented in figure 8. When size for additive particle of (P.F) ratio is changed we notice a change in the diametrical strength where large pores work to reduce the resistance of the load on them.

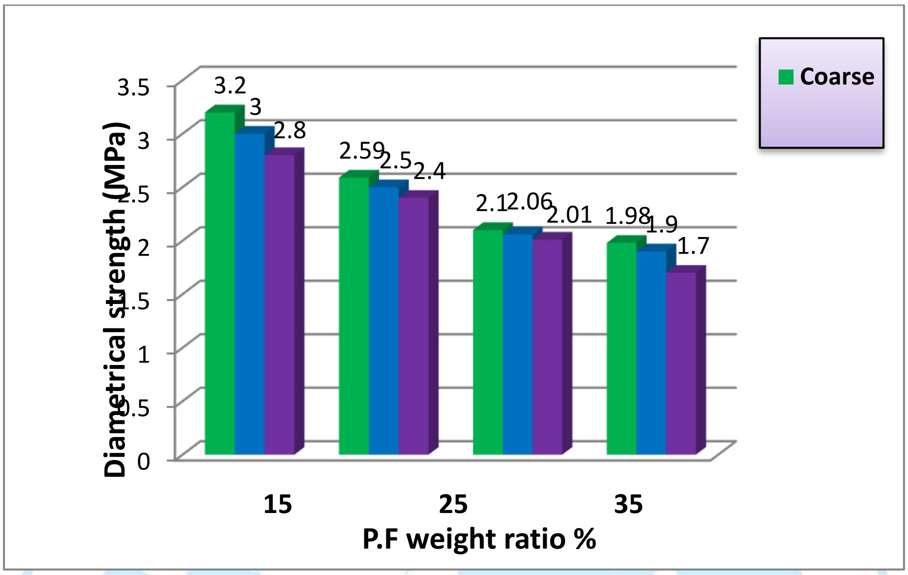

Figure 8: Effect of particle size on the diametrical strength of crude petroleum filters with ratios (15, 25, 35, and 45) %.

Crude petroleum:

Table 4: Physico-chemical Properties of Al-ahdab crude petroleum before immersion of crude petroleum filter balls.

Property	Value before Immersion of crude petroleum filter balls
API Gravity	24.70
Sulfur Content wt. %	3.76
Carbon residue wt. %	8.8
Asphaltene content wt. %	6.68
Metallic Content	
Vanadium content ppm	86
Nickel content ppm	32
Iron content ppm	0.73

Table 5: Physico-chemical Properties of Al-ahdab Crude petroleum after immersion of crude Petroleum filter balls for 14 days with P.F weight ratio30% from fine particle size

Property	Value after Immersion of crude Petroleum filter balls with30%fine (P.F) for14 days
API Gravity	32.5
Sulfur Content wt. %	2.6
Carbon residue wt. %	4.53
Asphaltene content wt. %	1.6
Metallic Content	
Vanadium content ppm	47.52
Nickel content ppm	11.43
Iron content ppm	1.32

Clays are played an important part in petroleum refining industry [11]. In the petroleum refining industry, various processes such as adsorption and separation are rapidly spreading. Many components can be removed by clay adsorption, such as sulfur, deasphalting, and heavy metals. Adsorption is one of the simplest and most effective separation methods used in different industries.

American Petroleum Institute (API) Gravity: Among the most important properties of crude oil, companies can use this property to identify the type of light or heavy petroleum, which is also an important property to determine the price of crude oil. The results demonstrate that the Al-ahdab crude oil is heavy oil and after immersion petroleum filter balls with (P.F) weight ratio 30% from fine particle size can transform to light oil.

Sulfur content: Sulfur compounds have to be removed from petroleum. These compounds cause several problems such as air pollution and corrosion of parts in engines [12, 13]. Desulfurization by adsorption of commercial kerosene and diesel oil causes increasing of the surface area and pore size.

Additionally, kaolin with improved surface morphology was selected to adsorb sulfur compounds in petroleum, so that it can interact more selectively with sulfur compounds.

Adsorption desulfurization depends on the ability of solid adsorbents to selectively adsorb organic sulfur compounds from oil. The efficiency of this method depends on the characteristics of the adsorbent material: relative to the selectivity, adsorption capacity, durability and reproducibility of hydrocarbons for organic sulfur compounds. Since the slurry can be considered an active adsorbent, the carbon residue is reduced, and the adsorption advantage is the reactive removal of organic matter with the weak Van der Waals forces.

Carbon Residue wt. %: Since the clays can be considered an active adsorbent, the carbon residue is reduced, also the adsorption proses is the reactive removal of organic matter which having the weak Vander Waals forces.

Asphaltenes content wt. %: Also, the Asphaltenes content decrease because Kaolin can be considered active adsorbent for asphaltenes, according to the polar sites in the kaolinite structure located on the broken edge and the exposed hydroxyl terminal plane [14, 15]. In petroleum asphaltenes consider to be the major source to several complications such as clogging of pipelines, surface facilities, pumps, safety valves and fouling, which can affect production, transportation, storage and the refinery processes. The most significant commercial application of adsorption is the removing of asphaltenes.

Metallic Content (Ni, V, and Fe): metal contents like vanadium, nickel and iron decrease because of adsorption process Clay adsorption can be played a significant role in the elimination of heavy metals [16, 17]. Demetallization, which has to do with the removal of these metal ions, is therefore to enhance efficiency in the crude oil.

This behavior can be explained based on the fact that metals (nickel and vanadium) are mainly present in crude oil in the form of porphyrin complexes, while porphyrin complexes are usually associated with asphaltene fractions. Therefore, the asphaltene aggregates must be broken to expose the metal ions for removal.

In all Crude petroleum result the crude petroleum filter balls with 30% fine (P.F) is the best because it produces very small pores ≅ 300 µm give a large surface area to the ceramic material therefore, achieved adsorption process with high efficiency.

Conclusions

Porous ceramic balls were prepared from the mixture (kaolin and alumina) by adding raw materials (P.F) in proportions (5, 10, 15, 25, 35 and 45) %. Due to the different shapes of the pores generated, the physical, mechanical and crude oil properties are affected by the addition ratio. After sintering at 1100 ° C, the fine volume (P.F) produces small closed cells. When the added amount is 45%, the minimum linear shrinkage rate reaches 7.7% (P.F). The addition of alumina enhances the formation of mullite and improves the physical, mechanical and crude oil properties of the prepared filter samples.

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