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# Organic Matter in Petroleum Sludges a Source of Useful Materials

## *Part 2:*

## Separation and Analysis of Petroleum Naphtha Soluble Fraction

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# المادة العضوية في المخلفات النفطية مصدر لمواد مفيدة

## الجزء الثاني:

## فصل وتحليل الجزء القابل للذوبان في النفثا البترولية

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تتمحور الدراسة حول فصل وتجزئة المادة العضوية في مخلفات (كدارة) خامي السدرة والحمادة باستعمال نفثا بترولية. يمتلك خاما السدرة والحمادة الصفات الفيزيائية والكيميائية المبينة أدناه على التوالي:

الكثافة بمقياس معهد البترول الأمريكي (API) = 37 و 39

المحتوى الكبريتي (S%) = 0.08 و 0.39

المحتوى النتروجيني (N%) = 0.06 و 0.17

محتوى المواد غير الذائبة في الهبتان الطبيعي (%n $C_7$ Insol) = 0.30 و 0.73

تم استعمال الأنواع التالية من النفثا البترولية في عملية الفصل:

نفثا خفيفة مجال درجة غليانها بين 20–50° م

نفثا ثقيلة مجال درجة غليانها بين 80–160° م

نفثا مصدرية نقية هي الهبتان الطبيعي درجة غليانها 101° م لغرض المقارنة.

أجريت عملية الفصل معملياً باستعمال نسبة مذيب إلى ترسبات بمقدار 1:25 وتم رج المزيج لمدة محدودة بواسطة الأمواج فوق الصوتية وحققت العملية فصل المادة المالتينية (الجزء المذاب في النفثا) حيث تم عزل المادة الأسفلتينية المتخلفة (الجزء غير المذاب في النفثا) بواسطة تقنية الطرد المركزي وتستخلص المالتين أخيراً بواسطة تقطير النفثا. شملت الدراسة تحليل نسب العناصر الرئيسية CHN وكذلك محتوى العناصر الثقيلة في جزء المالتين وبيّنت النتائج عند إستعمال النفثا الثقيلة في عملية الفصل أن 65% من مكونات المادة العضوية في كدارة خام الحمادة هي مادة مالتينية بينما ترتفع هذه النسب إلى 79% في مخلفات خام السدرة. عند محاولة فصل المادة العضوية الثقيلة من الجزء الأسفلتي بواسطة استخلاصها بالمذيب رباعي هيدروفيوران (THF) شوهدت مؤشرات قوية تدل على تفاعل المذيب مع المادة الإسفلتية في الكدارة وأدى هذا التفاعل إلى زيادة غير مألوفة في ناتج الفصل بلغت أضعاف ما كان متوقعاً وهذه الظاهرة لم تحدث عند استعمال مذيب أروماتي هيدروكربوني مثل التلوين في عملية الفصل. من المتوقع أن يكون لهذه الظاهرة مردودات تطبيقية وتتطلب دراسة خاصة بها.

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**Abstract:** *The organic matter in sludges from two Libyan crude oils [Sedra, API = 37, S = 0.39%, N = 0.17%, n -C7 insolubles = 0.73%; and Hamada, API = 39, S= 0.08%, N = 0.06%, n - C7 insolubles = 0.3%] were sub-fractionated with light naphtha (LN, boiling range 20 - 50°C) and heavy naphtha (HN, boiling range 80 - 160°C). A reference fractionation with n-heptane (HEPT = boiling point 101°C) was also conducted for comparison purposes. Solvent to sludge ratio was 25 : 1 and agitation was performed supersonically. The separation of undissolved asphaltics was achieved by centrifugation.*

*Results are presented on fractionation of organic matter, elemental analysis of maltenes and determination of ash and heavy metal contents in the fractions.*

*Average values of 65% and 79% of total sludge weight was separated as a maltene fraction from Hamada and Sedra sludges respectively, using heavy petroleum naphtha as a solvent.*

*Extraction of organics from the asphaltic portion with tetrahydrofuran resulted in a several folds increase in the expected yield of organics, indicating reaction with the solvent. No such reaction took place when the extraction was performed using toluene.*

## INTRODUCTION

Sludge material depositing in storage tanks over the years represents net loss of valuable resources. It also reduces the storage capacity of the storage installations and has to be removed periodically. If sludge material is not processed into useful feeds or products, it will impart a heavy burden on oil industry and on the environment. Composition of sludges from storage tanks of various crude oils has been reported [1,2,3,4]. Solvent fractionation of sludges from waxy crude oils also was investigated [5]. The motives and aims of this study were reported in Part 1 [6b]. Fractionation of toluene soluble organics, extracted from sludge deposits in Part 1, was conducted using alkane solvents: n-pentane and n-heptane. Analysis of sludge in terms of water and inorganic contents and distribution of heavy metals in the sub-fractions were also assessed in that part of the study.

In the present work a more applied motivated approach was investigated to effect the fractionation of sludge matter into major fractions, namely: Maltenes and Asphaltics, using locally produced petroleum naphtha. The diagram (Fig. 1) illustrates the fractionation scheme used in our investigation. The results of this study were partly presented in a conference in Egypt [7].

## EXPERIMENTAL

### *Materials and Instruments:*

- Light naphtha was obtained from Az Zawiyah refinery, and was expected to possess a boiling range of 30 - 80°C; however the boiling point never exceeded 45°C, when the solvent was recovered after use.
- Heavy naphtha was obtained from Az Zawiyah refinery, and possessed a boiling range of 80 to 160°C.
- Normal heptane (n-C7), boiling point 101°C was obtained from Aldrich Chemical Company.
- Centrifuge used was: Seta - Iec, Oil test centrifuge.
- Supersonic vibrator used was: Karl Kolb, Telsonic D - 6072
- C, H, N analyzer used was: Carlo Erba Strumentazione MOD 1106.
- Sulfur was determined by HORIBA SLFA - 1100 method.
- Heavy metals were determined by atomic absorption spectroscopy using a spectrophotometer model VARIAM A.A. 1475.

### *Experimental Procedures*:

**1.** ***Separation of maltenes from sludge:***

Toluene (20 ml) was added to 20 g, accurately weighed sludge in a 1000 ml conical flask. The mixture was warmed to 60°C with shaking. The naphtha solvent (500 ml); LN, HN or n-HEPT, was added (in three separate determinations) and the whole mixture was supersonically shaken for 2 h in a water bath at 60°C. After this, the mixture was centrifuged 15 minutes at 2000 rpm in a suitable centrifuge. The upper layer containing the dissolved maltenes was decanted into a distilling flask, followed by distillation of solvent and determination of maltenes yield.

The insoluble asphaltic portion was transferred by a spatula from the centrifuge tubes to a labeled sample jar.

**Table 1. Analysis of Hamada and Sedra crude oils performed by SGS.**

| Property | Crude oil and value | | Method of analysis |
|---|---|---|---|
| | Hamada | Sedra | |
| Density, 15.5°C, (g.ml$^{-1}$) | 0.8296 | 0.8395 | IP 365/D 4052 |
| API gravity, 15.5°C | 38.98 | 37.00 | Calculated |
| Total sulfur, (wt.%) | 0.08 | 0.39 | IP 336/D 4294 |
| Total nitrogen, (wt.%) | 0.06 | 0.17 | IP 379 Mod./D 462g Mod |
| Asphaltenes, (wt.%) | 0.25 | 0.53 | IP 143 |
| n-Heptane insolubles, (Wt.%) | 0.30 | 0.73 | D 893 |
| Ash content, (wt%) | <0.01 | <0.01 | IP 143 |
| Vanadium,(ppm) | 1.6 | 2 | IP 377 Mod |
| Nickel,(ppm) | 1.1 | 7 | IP 377/Mod |

**Table 2. Separation of maltenes from Hamada and Sedra sludges with petroleum naphtha and n-heptane.**

| Name of sludge and No. of determinations | Percent soluble maltenes | | |
|---|---|---|---|
| | Light naphtha | Heavy naphtha | n-heptane |
| Hamada<br>1<br>2<br>3 | <br>60.20<br>58.56<br>49.26 | <br>61.62<br>72.56<br>62.21 | <br>68.77<br>70.05<br>73.22 |
| Average<br>(S.D.) | 56.01<br>(± 5.90) | 65.46<br>(± 6.45) | 70.68<br>(± 2.23) |
| Sedra<br>1<br>2<br>3 | <br>51.95<br>49.85<br>55.00 | <br>72.40<br>84.33<br>80.64 | <br>72.76<br>75.74<br>78.17 |
| Average<br>(S.D.) | 52.23<br>(± 2.59) | 79.12<br>(± 6.07) | 75.56<br>(± 2.70) |

2. ***Separation of organics from asphaltics by tetrahydrofuran and by toluene:***

A sample of about 2 g of mixed Hamada and Sedra asphaltics (accurately weighed to three decimals) was extracted with 100 ml of THF (or Toluene) in a soxhlet system. The extraction was continued until complete discoloration of the extracts, (2 h in case of THF and 4 h in case of Toluene). The solvents were then removed by distillation, followed by drying for 2 h at 105°C. The weight of extracted organics was determined and their percentage was calculated.

Inorganics in the thimble were determined by drying and weighing the thimble.

## RESULTS

In the beginning, some of the analysis results of Hamada and Sedra crude oils that are of relevance to our work are listed in Table 1. The analysis was conducted by the English consultant company SGS [8].

The results of separating the maltenes from the two sludges using light and heavy petroleum naphtha are given in Table 2.

The ultimate analysis (C, H, N, S & O) of maltenes separated by the three solvents LN, HN and HEPT from Hamada and Sedra sludges are given in Table 3.

**Table 3. Elemental analysis of maltenes separated by LN, HN and HEPT from Hamada and Sedra sludges.**

| Source of maltenes | % C | % H | % N | % S | % O(1) | H/C ratio |
|---|---|---|---|---|---|---|
| HM(2) LN | 74.22 | 11.33 | 1.05 | 1.172 | 12.23 | 1.83 |
| HM HN | 79.88 | 12.46 | 0.85 | 0.988 | 5.82 | 1.87 |
| HM HEPT | 81.27 | 12.58 | 1.08 | 1.066 | 4.00 | 1.86 |
| SM(3) LH | 80.55 | 12.43 | 0.88 | 1.170 | 4.97 | 1.86 |
| SM. HN | 81.27 | 12.02 | 0.85 | 0.845 | 5.02 | 1.78 |
| SM HEPT(4) | 79.28 | 12.32 | 0.99 | 1.052 | 6.36 | 1.86 |

1- Calculated by difference.
2- HM = Hamada maltenes.
3- SM = Sedra maltenesSM.
4- HEPT = Sedra maltenes soluble in n-heptane.

Detailed analyses of ash and heavy metals content in maltenes separated by the three solvents from Hamada and Sedra sludges are given in Table 4.

**Table 4. Ash and heavy metals content in maltenes separated from Hamada and Sedra sludges.**

| Maltenes sample | % Ash | Trace heavy metals, (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | V | Ni | Zn | Mn | Pb | Cu | Fe |
| HM. LN | 0.0/ | 0.9 | 0.6 | 4.0 | 0.5 | 30.5 | n.d(*) | 10.5 |
| HM. HN | 0.88 | 3.0 | 2.1 | 14.4 | 2.3 | 182.3 | n.d. | 101.8 |
| HM. HEPT | 0.56 | 1.8 | 1.0 | 7.0 | 1.0 | 82.3 | n.d. | 52.6 |
| SM. LN | 0.01 | 0.5 | 0.4 | 0.8 | 0.2 | 11.2 | 0.5 | 1.6 |
| SM. HN | 0.31 | 1.2 | 3.4 | 13.5 | 8.2 | 3.1 | 4.8 | 99.7 |
| SM. HEPT | 0.18 | 1.2 | 2.3 | 9.4 | 4.4 | 3.2 | 3.4 | 74.4 |

(*) n.d = not determined.

The results on the separation of organics from the mixed Hamada and Sedra asphaltics by terahydrofuran are given in Table 5.

**Table 5. Separation of organics from mixed asphaltics by THF and toluene.**

| Type of mixed asphaltics | % Organics | % Inorganics | Remarks |
|---|---|---|---|
| [H+S]. As. LN (*) | 452(1)<br>313(2)<br>256(3) | 2.19<br>–<br>0.80 | (1), (2), (3), Increase in yield registered by three different operators |
| [H+S]. As. HN | 369<br>99.3(4) | 2.39<br>1.80 | (4) Separation by toluene |
| [H+S]. As. HEPT | 279 | 1.38 | |

(*) [H+S]. As. LN = Mixed Hamada and Sedra asphaltics separated by light naphtha.

## DISCUSSION

### Maltenes Yield:

Factors affecting the yield of maltenes extraction from the sludges under investigation are:

1- The chemical composition of the parent crude oils, mainly in terms of sulfur, nitrogen, asphaltenes and heavy metals contents.

2- The physical characteristics of the parent crude oils, mainly density expressed as API gravity value.

3- The boiling range of naphtha used in extracting the maltenes from the sludge.

4- The degree of homogeneity of the sludge components (i.e. bitumen, fines and water).

5- Time of exposure of the sludge to the atmospheric conditions (i.e. age of sludge). Aged sludge is expected to be more oxidized, containing more fines, asphaltenes and water and thus less maltenes.

Inspection of the data in Table 1 affords information on the physical and chemical characteristics of the parent crude oils. The interaction between factors 3 through 5 mentioned above, taking into accounts the basic characteristics in factors 1 and 2, gave the results shown in Table 2 on the yields of extracted maltenes. These results might be further explained as follows:

In line with the API gravity and chemical composition of Hamada and Sedra parent crudes, the average yield of light naphtha extracted Hamada maltenes was higher than that of Sedra [cf. HM.LN = 56.01% Vs SM.LN = 52.23%].On the other hand, when heavy naphtha is concerned, the trend is altered with a much more pronounced difference [c.f. SM.HN = 79.12% Vs HM.HN = 65.46%; and HM.LN = 56.01% Vs HM.HN = 65.46%; and SM.LN = 52.23% Vs SM.HN = 79.12%].Thus the higher the boiling range of the naphtha the higher the yield of the maltenes. This is in fact expected in the light of increased solubility of higher homologues at higher temperatures and higher molecular weight of the solvent [9a and b,10].

In the case of maltenes extraction with n-heptane, where the solvent is possessing an intermediate molecular size and boiling point as compared to LN and HN, the results indicated inverse relationship with API [c.f. HM.HEPT = 70.68% Vs SM.HEPT = 75.56%].We believe that the most likely reason for this is factor 4, related to incomplete homogeneity of the analyzed samples. It was mentioned in Part 1 [6] that it was very difficult to homogenize the sample because of its extreme high viscosity and the separation of pools of viscous oil and some floating water on cooling to room temperature.

### Maltenes Analysis:

The results of elemental analysis are given in Table 3. Main observations from these results on aspects related to the chemical nature of maltenes separated by the three solvents, are the following:

1- Except the slightly different case of SM.HN, the H/C ratio is about identical in all maltenes. Also the value of this ratio of all maltenes samples being approximately 2, reflects the predominance of the saturation nature of carbon to carbon bond in these maltenes.

2- About 13 folds increase is observed in the sulfur content of HM compared to the parent Hamada crude oil (refer to Table 1).

3- In a similar comparison as in 2 above, with respect to nitrogen content, the values of 15 and 5.3 fold increase are found in HM and SM respectively compared to the parent crude oils.

These observations on the increased magnitudes of S,N and most probably O(calculated by difference) in the sludge maltenes, further supplement the previously suggested mechanism [6a] for the sludge separation and deposition. It was suggested then, that the most polar species containing S,N,O, etc, are attracted to salt saturated, water droplets suspended in the parent crude oil. The coalescence of these droplets and the effects of gravitational pull on them results in sludge accumulation at the bottom, comprising the most polar and the most heavy constituents of petroleum.

The analysis of ash and heavy metal contents in the maltenes separated by the three naphtha solvents are given in Table 4 and plotted in figures 1 and 2. It is clear that maltenes separated with light naphtha from the two sludges (HM.LN and SM.LN) contain about 100 ppm of total ash with relatively low concentrations of V, Ni, Mn and Fe as compared to the case of separation by heavy naphtha (HM.HN and SM.HN).

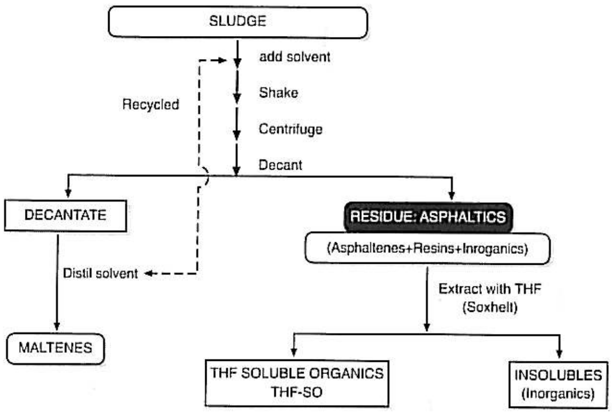


Fig. 1. Solvent fractionation of sludge deposits using petroleum naphtha.

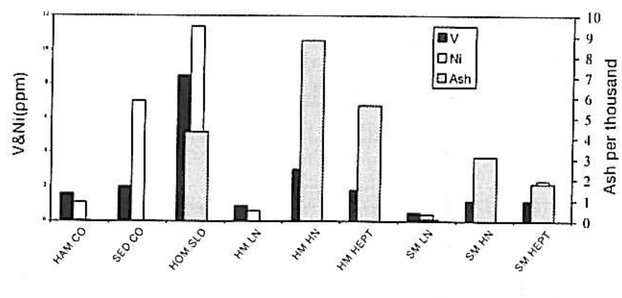


Fig. 2. Ash, vanadium and nickel distribution in crude oil, homogenized sludge and maltenes.

The analysis of heavy metals content showed a noticeable increase of Pb in HM and of in both HM and SM. Similar trend was also observed for Mn and Zn in both HM and SM. Tentative explanation of these increments may partly be due to contamination of sludge by ions released to it as a resulf of corrosion of the storage tanks internal metallic surface. The building materials of crud oil storage tanks are usually alloys of iron with some of the above mentioned heavy metals. Corrosion usually occurs when protection against it is inadequate.

A comparison is given in Table 6 between ash and some of the heavy metal contents in HM and SM separated by petroleum naphtha and their contents in a homogenized 50% Hamada + 50% Sedra sludge [6a and b] and in parent crude oils [8].

**Table 6: Ash vanadium and nickel contents in homogenized sludge and parent crude oils.**

| Type of sample | Percent ash | V (ppm) | Ni (ppm) |
|---|---|---|---|
| Homogenized sludge | 4.31 | 8.50 | 11.40 |
| Hamada crude oil* | < 0.01 | 1.60 | 1.10 |
| Sedra crude oil* | < 0.01 | 2.00 | 7.00 |

(*) Analyzed by SGS.

It is obvious from Tables 3, 4 and 6 and Figure 2 that a noticeable reduction in ash and heavy metals contents occurred in the maltenes separated by heavy naphtha from the two sludges under investigation. With respect to V and Ni contents, the corresponding sludge maltenes contains twice as much as the parent crude oils. On the other hand separation of maltenes by light naphtha yields heavy metals and ash contents comparable with their contents in the parent crude oils.

One last observation, on the heavy metals analysis of maltenes separated by n-heptane (both HM.HEPT and SM.HEPT) that, ash and heavy metal concentration values are intermediate between the values obtained by LN and HN. This in fact is expected to be dependant on the molecular size of the three solvents used in separating the maltenes. In other words, higher molecular weight solvents are expected to dissolve higher molecular weight resinous type materials with their higher metallic contents [10].

For efficient stripping of asphaltenic compounds from the inorganic constituents in the asphalt portion obtained after the separation of maltenes, tetrahydrofuran (THF) was used to accomplish this purpose. The results are given in Table 5. Mixed Hamada (H) and Sedra (S) asphaltics were used and the yield of organics (asphaltenes and some resinous compounds) increased several folds on what was expected. The reaction with the solvent; by a mechanism which is until now not understood; is the only possible cause for the weight increase.

No such increase in weight occurred when the extraction was carried out using toluene ($C_7H_8$) instead of THF. The following points need further investigation on this unexpected phenomenon:

- The nature of the yield and whether polymerization of the solvent is a part of the reaction taking place.
- Is the reaction catalyzed by the indigenous inorganic constituents in the asphaltics portion?
- Is the new product beneficial for any use in the petroleum and other operations?

## CONCLUSIONS

Higher boiling petroleum naphtha produced a noticeable increase in the amount of separated maltenes compared to the case of separation by light naphtha. The average percentage increase was 9.5% and 16.9% for Hamada and Sedra sludges respectively.

The several fold increase in the heteroatom contents (S,N and O) in sludge maltenes compared to the original parent crude oil suggests a peculiar mechanism; in line with that proposed in Part 1; for the separation and deposition of sludge at the bottom of storage tank.

The H/C ratio being approximately 2 reflects the predominance of the saturation nature of the C-C bond in these maltenes. The value of 1.78 for this ratio in SM.HN indicates a relatively higher aromatic carbon content in this maltene.

Maltenes separated by light naphtha showed ash and heavy metals contents comparable to the parent crude oils, while separation by heavy naphtha produced maltenes of higher ash content and about twice as much of V and Ni as in the parent crudes.

Most relevant conclusion from this work is that: about 70% of the organic matter in the studied sludges is of maltenic nature, which can be easily separated by petroleum naphtha. The separated maltenes can be blended with gas oil naphtha to produce a good quality fuel oil. Alternatively, blending a petroleum naphtha sludge maltenes, in a predetermined ratio, with a compatible exported crude oil may represent another way of reclaiming this polluting material.

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