



# Removal of Vanadium and Nickel Ions from Iraqi Atmospheric Residue by Using Solvent Extraction Method

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## Abstract

Iraqi crude Atmospheric residual fraction supplied from al-Dura refinery was treated to remove metals contaminants by solvent extraction method, with various hydrocarbon solvents and concentrations. The extraction method using three different type solvent (n-hexane, n-heptane, and light naphtha) were found to be effective for removal of oil-soluble metals from heavy atmospheric residual fraction. Different solvents with using three different hydrocarbon solvents (n-hexane, n-heptane, and light naphtha) .different variables were studied solvent/oil ratios (4/1, 8/1, 10/1, 12/1, and 15/1), different intervals of perceptual (15, 30-60, 90 and 120 min) and different temperature (30, 45, 60 and 90 °C) were used. The metals removal percent were found depending on the yield of asphaltene. The solvent-oil ratio had important effects on the amount of metal removal. The metals removal was increased at increasing temperatures from 30 to 90 °C increases the metal ion precipitated. The highest Ni precipitated was 79.23 ppm using heptane at 90 °C while for V the highest value was 64.51 ppm using also heptane at 90 °C, while the mixing time decreased metals removal. With increasing asphalt yield, the removal of metal was more selective. Among the solvents used in the extraction treatment method, the highest Ni precipitated was 76 ppm using hexane at 150 ml solvent and showed the most promising results. Increasing mixing time increases metals removal for V, the highest value was 65.51 ppm using either heptane or light naphtha.

The highest Ni precipitated was 78 ppm using heptane at 120 min while for V the highest value was 67 ppm using either heptane or light naphtha after 120 min.

*Keywords: metal removal, atmospheric residue, deasphalting process, solvent extraction*

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## 1- Introduction

In response to the global energy consumption needed, the oil refining industry has been developing new ways to overcome asphalt-bearing streams and metal-containing strips with growing efforts and resources [1]. Crude oils normally have various quantities of impurities, not metal and metal. Non-metallic impurities typically include nitrogen, sulfur, and oxygen; nickel, vanadium, iron, sodium, copper, zinc and arsenic are usually metallic impurities [1].

Deasphalting is a traditional selective extraction process, which is designed to separate by a suitable solvent a portion suited for deasphalted oil conversion (DAO) and a portion suitable for thermal conversion (pitch)[2]. The strong atmospheric residue is asphalt that depends on the form of solvent that is used [3].

The unit throughput is limited by a growing number of asphalt compounds in the feed. Asphaltene can also contain a considerable amount of sulfur, nitrogen, and metals, and/or fraction thereof. The majority of the raw oil content of the refineries can be concentrated and/or collected in feed for the hydroconversion units [4].

Solvent deasphaltation is a commercially performed method for extracting asphalt from the heavy oil from the ambient and/or vacuum towers.

The solvent deasphalt unit requires high capital costs and high operating costs for solvent recycling [5].

Solvent deasphalting (SDA) is a special method in which the remains are broken into a low contaminant deasphalted oil (DAO) rich in paraffin, using the molecular weight (density) rather than the boiling spot. It is a relatively cheap method that has reasonable versatility to achieve a wide variety of DAO qualities[6]. A solvent (typically C3–C7) is employed and retrieved by supercritical recovery methods from both substance streams (atmospheric and vacuum distillation)[7].

During the solvent deasphalting phase, the solvent solution is solvent dependent on the application of paraffin (C4–C7) solvents (butane, pentane, hexane, and heptane). The insoluble pitch is precipitated as asphalt from the mixed feedstock. The extractor separates the deasphalted oil phase from the pitch phase. The extractor is designed to separate the two phases efficiently and reduce contaminant entry during the DAO process [8].

As a result of its low metal content (ni and V), DAO is usually used as the fluid catalytic FCC cracker or a hydrocracker feedstock. SDA technology can be used in many ways that allow the refiner to progressively move towards the development of zero fuel oil residues over time[9].

Most of the metal pollutants are considered to be found in the production of waste crude oil as inorganic sulfides, oxides, and water-soluble constituents. The remaining metals are commonly concentrated in the residual fractions of oil as relatively thermally stable, oil-soluble organometallic structures such as metal porphyrins and derivatives [10, 11, and 12]. Now the toxic effects of petroleum metals have been recognized.

The metals do not contaminate the product only, but the metals contaminate the products, but even the metal chelates cause catalytic toxicity and excessive gas and coke formation. The corrosion of fuel oil burning facilities also causes significant harm to vanadium and nickel along with sodium [13].

The high levels of metal of petroleum residues currently need expensive improvements, both by high hydrogen adjustment costs and by high carbon discharge losses. If metal was extracted before the conventional hydrocracking process in a pretreatment stage, the residues could be improved more economically [14, 15].

The work aims to study different conditions such as asphaltene yield, time, solvent types, solvent ratio, and temperature on the Removal of vanadium and Nickel ions from Iraqi heavy crude oil.

## 2- Experimental Work

This study discusses the removal of metals from the residual fraction using a relatively solvent extraction method. The solvents used are (n-hexane, light naphtha, and n-heptane) in this study, different solvent/oil ratios (4/1, 8/1, 10/1, 12/1, and 15/1), different perceptual periods (15, 30, 60, 90, and 120 min) and different temperatures (30, 45, 60 and 90 ° C).

The sample of atmospheric residue from the AL-Dura refinery was treated with a variety of chemical solvents to remove metals (Ni, V).

### 2.1. Materials

Three types of petroleum solvents were used in this study and the Atmospheric residue:

#### a. Atmospheric Residue

Table 1 displays the characteristics of Iraqis atmospheric petroleum-residues supplied from Al-Dura refinery oil residues.

Table 1. The properties of atmospheric oil residue

Characteristics	value
Specific gravity at 15.6/15.6 °C	0.9705
API gravity	14.9
Kinematic viscosity, c.st.at 100 °C	32.73
Sulfur content, wt. %	0.5
Flashpoint °C	190
Vanadium content, wt. ppm	86.14
Nickel content, wt. ppm	79.6

#### b. Hydrocarbon Solvents

##### b1- n-hexane

n-hexane with a purity of 99% was supplied from MERCK

##### b2- n-heptane

n-heptane with purity 99% was supplied from (POCH SA) company.

##### b3- Light naphtha

Light naphtha with 99% purity was supplied from the AL-Dura refinery.

### 2.2. Experimental Laboratory Setup

The deasphalting laboratory device represents in Fig. 1 which is used to measure the metal removal consists of mixing of oil residuals (and solvents) in two-neck flask glasses with solvent /oil ratio of 4/1, 8/1, 10/1, 12/1, and 15/1, round flask put in a magnet heating stirrer with a speed of 450 to 120 rpm and a temperature range from 30 to 220°C, and a perceived length of 15, 30, 60, 90 and 120 min.

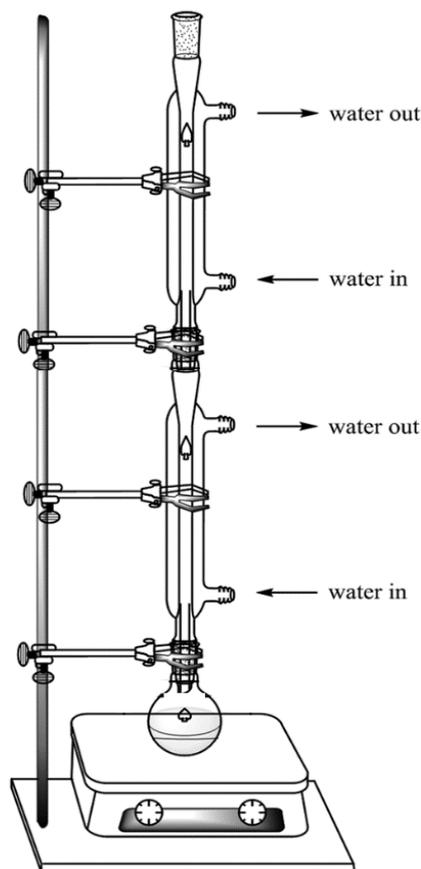


Fig. 1. The de asphalting apparatus and its scheme

The sample was transferred to a 5 mm Hg vacuum filter pump represented in Fig. 2. On a filter paper surface to which it has been weighted in size, the solvent and the residual filtrate persist through the flask and asphalt.

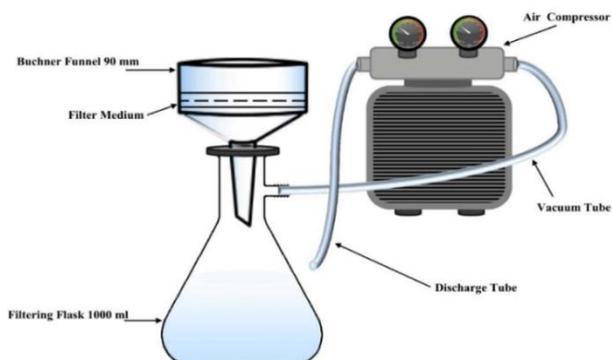


Fig. 2. Filtration unit setup

To measure the metal content of the sample, one gram was dried and treated with 750 °C in the oven for 30 min then the sample was cooled at room temperature. After cooling the sample was mixed with 5 ml of concentrated hydrochloric and nitric acid each and then placed in the oven at 150 °C for 15 min after sample preparation it was taken to 25 ml bottle and the sample is ready to be tested for metal content using Analytikjena AA NOV350.

### 3- Results and Discussion

#### 3.1. Effect of Solvent Type

The results of different parameters on metals removal are shown in Fig. 3 to 14. The effective parameters of the process included temperature, solvent to oil ratio, duration time, and asphaltene yield on metals content (Vanadium and Nickel). Fig. 3 and Fig. 4 show the effect of temperature on the metal ion for both Ni and V where the increase of temperature from 30 to 90 °C increases the metal ion precipitated. The highest Ni precipitated was 79.23 ppm using n-heptane at 90 °C while for V the highest value was 64.51 ppm using also heptane at 90 °C Fig. 5 and Fig. 6.

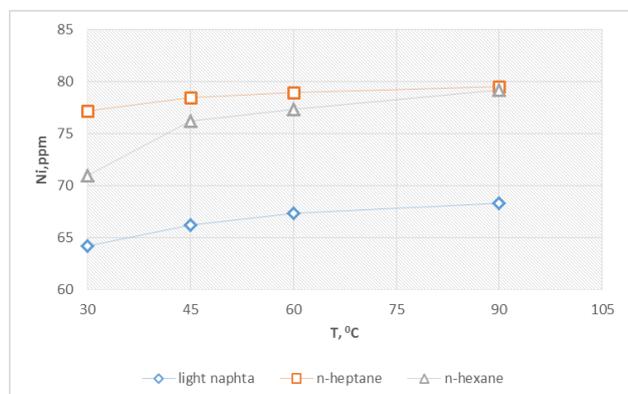


Fig. 3. Effect of temperature on Ni metal ion using different solvent at 450 rpm, 15/1 solvent to oil ratio, and 120 min

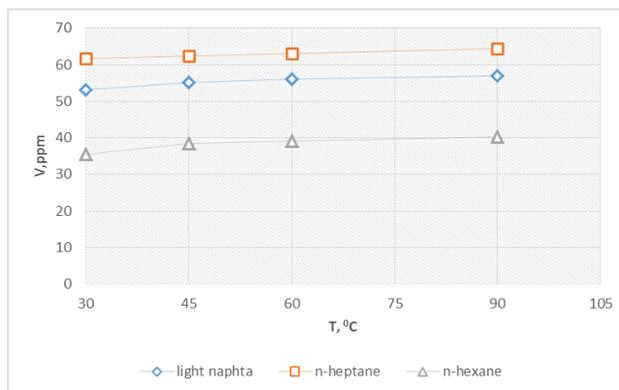


Fig. 4. Effect of temperature on V metal using different solvent at a different temperature at 450 rpm, 15/1 solvent to oil ratio, and 120 min

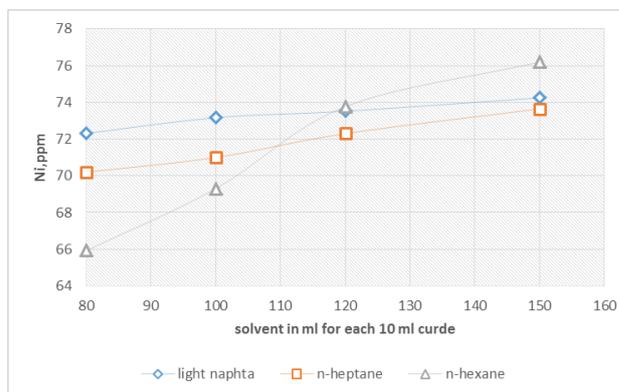


Fig. 5. Effect of solvent to oil ratio on Ni metal ion using different solvent at 450 rpm, 90 °C, and 120 min

The effect on the reduction of vanadium and nickel respectively of the increase in the solvent ratio is demonstrated. In this case, the rising proportion of solvents contributed to a greater decrease in metals due to increased asphalt removal. Since the Paraffin solvent capable of soluble oil paraffin, it cannot solubly asphalt is the solvent was able to enhance the properties of DAO [16]. The highest Ni precipitated was 76 ppm using hexane at 150 ml solvent while for V the highest value was 65.51 ppm using either heptane or light naphtha.

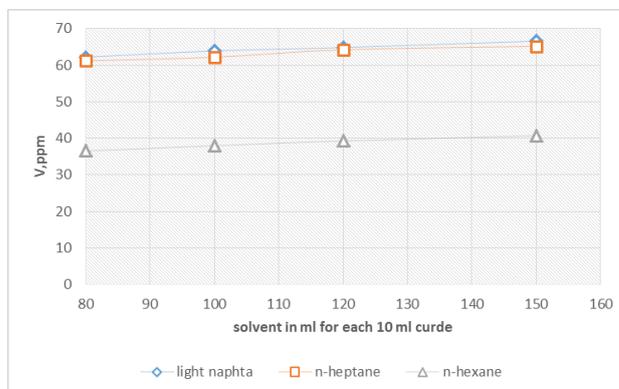


Fig. 6. Effect of solvent ratio on V metal ion using different solvent at 450 rpm, 90 °C, and 120 min

The effect of treatment time with different solvent types was also been studied for metal ion removal. Fig. 7 shows the Ni removal with time and in general as time increases the metal concentration in the process also increases. The reason for this phenomenon is the more mixing time for the solvent to penetrate the heavy composition of the asphaltene allowing the metal to precipitate [17]. The highest Ni precipitated was 78 ppm using heptane at 120 min while for V the highest value was 67 ppm using either heptane or light naphtha after 120 min.

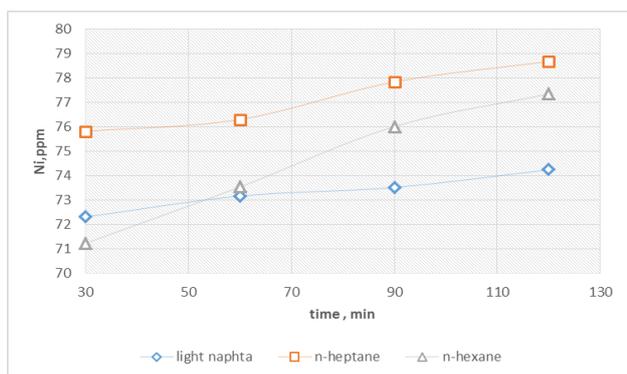


Fig. 7. Effect of duration time on Ni metal ion using different solvent at 450 rpm, 90 °C, and 15/1 solvent to oil ratio

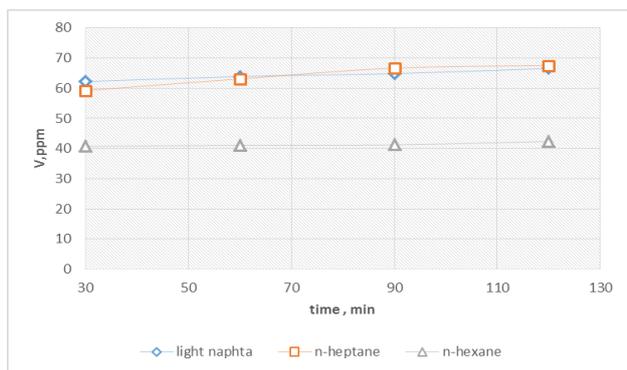


Fig. 8. Effect of duration time on V metal ion using different solvent at 450 rpm, 90 °C, and 15/1 solvent to oil ratio

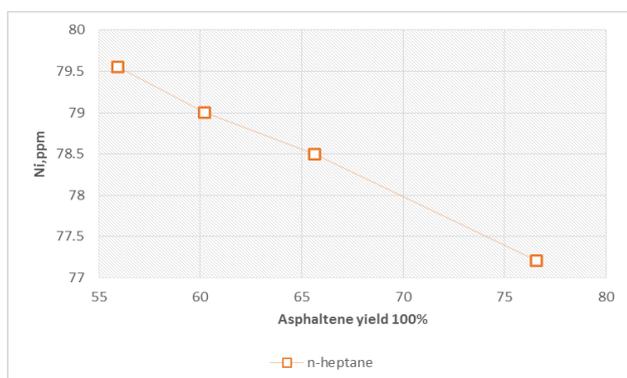


Fig. 9. Effect of asphaltene yield on Ni metal ion using heptane. at 450 rpm, 90 °C and 15/1 solvent to oil ratio, 120 min

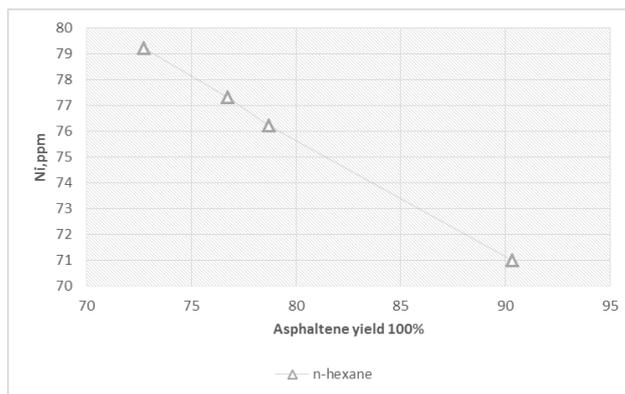


Fig. 10. Effect of asphaltene yield on Ni metal ion using hexane at 450 rpm, 90 °C, and 15/1 solvent to oil ratio, 120 min

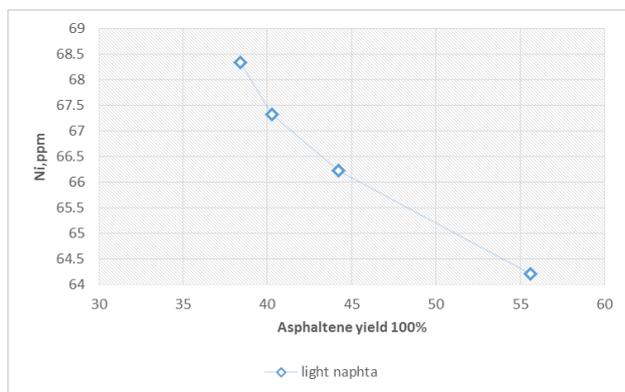


Fig. 11. Effect of asphaltene yield on Ni metal ion using light naphtha. at 450 rpm, 90 °C and 15/1 solvent to oil ratio, 120 min

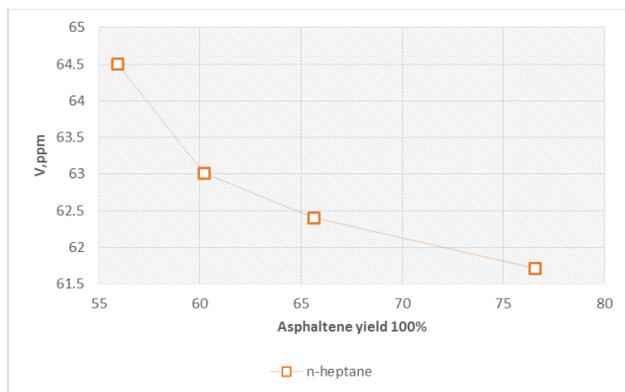


Fig. 12. Effect of asphaltene yield on V metal ion using heptane at 450 rpm, 90 °C, and 15/1 solvent to oil ratio, 120 min

Changes in the asphaltenes yield influence metal removal because such heteroatoms concentrate and isolate the DAO low heteroatoms formed in asphalt particles. Figures 9 to 14 show an improvement in asphaltene production in Ni and vanadium removal.

The increase in asphalt yields tends to contribute to the removal of high metals. The results showed that the decomposition process was selective for the removal of metals as well.

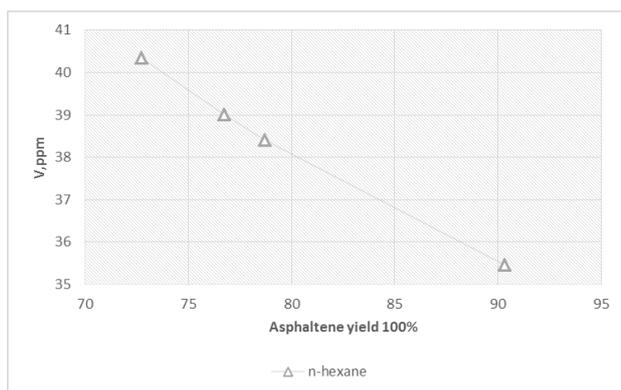


Fig. 13. Effect of asphaltene yield on V metal ion using hexane at 450 rpm, 90 °C and 15/1 solvent to oil ratio, 120 min

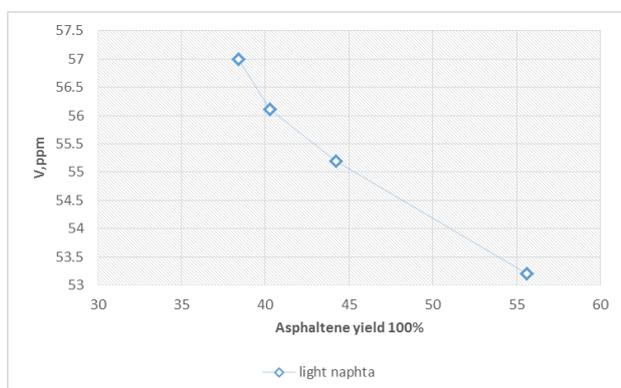


Fig. 14. Effect of asphaltene yield on V metal ion using light naphtha at 450 rpm, 90 °C, and 15/1 solvent to oil ratio, 120 min

#### 4- Conclusions

For the solvent extraction method in the asphaltene separation process, all solvents used were highly efficient on metal removal. The metal removal depended on the type of solvent and increased when the solvent chain length decreased. The solvent to oil ratio had a strong effect on the metal precipitated. The output of metal was increased at decreasing temperatures and the maximum output was obtained at 90 °C. The removal of metals was more selective as the asphaltene yield increased. Maximum efficiency of deasphalting, with n-heptane as the solvent, Ni precipitated was 79.23 ppm using heptane at 90 °C while for V the highest value was 64.51 ppm using also heptane at 90 °C.

#### Nomenclatures and Abbreviations

Parameter	Meaning	Unit
V	Vanadium	ppm
Ni	Nickel	ppm
DAO	Deasphalted oil	ml
SDA	Solvent deasphalting	Wt. %
FCC	fluid catalytic cracking	-
ppm	Part per million	-

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## إزالة أيونات المعادن من متبقي النفط الجوي العراقي باستخدام طريقة الاستخلاص بالمذيبات

نهى محسن علي داود و طارق محمد نايف

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### الخلاصة

تمت معالجة المتبقي من برج التقطير الجوي للخام العراقي المزود من مصفى الدورة لإزالة الملوثات المعدنية بطريقة الاستخلاص بالمذيبات. تم استعمال طريقة الاستخلاص باستخدام ثلاثة أنواع مختلفة من المذيبات (الهكسان و الهبتان والنافتا الخفيفة). تم استخدام كميات مذيبات بنسب مذيبات / الزيت (1/4 ، 1/8 ، 1/10 ، 1/12 ، 1/15) ، وفترات خلط (15 ، 30-60 ، 90 و 120 دقيقة) ودرجات حرارة (30 ، 45 ، 60 و 90 درجة مئوية). تم ايجاد ان نسبة إزالة المعادن تعتمد على ناتج الأسفلتين. كان لنسبة المذيبات إلى الزيت تأثيرات مهمة على كمية المعادن المزالة. زادت نسبة إزالة المعادن عند رفع درجات حرارة من 30 إلى 90 درجة مئوية مما يؤدي إلى زيادة ترسيب أيون المعدن. كان أعلى ترسب نيكل 79.23 جزء في المليون باستخدام الهبتان عند 90 درجة مئوية بينما كانت أعلى قيمة للفناديوم 64.51 جزء في المليون باستخدام الهبتان أيضاً عند 90 درجة. من بين المذيبات المستخدمة في طريقة الاستخلاص ، كان أعلى ترسيب هو النيكل بتركيز 76 جزء في المليون باستخدام الهكسان عند 150 مل من المذيب. بينما كانت أعلى قيمة للفناديوم 65.51 جزء في المليون باستخدام الهبتان أو النافتا الخفيفة. أعلى ترسب نيكل كان 78 جزء في المليون باستخدام الهبتان عند 120 دقيقة بينما أعلى قيمة للفناديوم كانت 67 جزء في المليون باستخدام الهبتان أو النافتا الخفيفة بعد 120 دقيقة.

الكلمات الدالة: إزالة المعادن ، متبقي النفط الجوي ، عملية ازالة الأسفلت والاستخلاص بالمذيبات