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SYNERGISTIC EXTRACTION OF VANADIUM BY DI-2-ETHYL HEXYL PHOSPHORIC ACID AND TRIBUTYL PHOSPHATE FROM BLACK SHALE SEDIMENTS, QUSEIR, RED SEA, EGYPT

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ABSTRACT

Extraction of vanadium from the sulphate leach liquor of the black shale from Nakheil mine NW Quseir, red sea, Egypt was studied by using a synergistic mixture of di-(2-ethylhexyl) phosphoric acid (DEHPA) and tributyl phosphate (TBP) in kerosene. A technological sample of this ore material assaying about 2400 $\mu\text{g/ml}$ V, 2300 $\mu\text{g/ml}$ Zn, 570 $\mu\text{g/ml}$ Mo, 1.6 % Fe and 272 $\mu\text{g/mL}$ Ni was collected for the present work. Metallic iron powder was found greatly an advantage to minimize the iron co-extraction, while adjusting the pH of aqueous solution to 0.8 minimized the co-extraction of Zn and Ni. The relevant extraction factors affecting maximum recovery of vanadium have been studied; namely solvent ratio (DEHPA/TBP), concentration of solvent, O/A phase ratio, contact time, settling time, temperature, the amount of reducing agent and the time of reduction. Selective stripping of vanadium has been performed using 100g/L Na_2CO_3 while Mo was left in the organic phase. The relevant stripping factors affecting maximum stripping of vanadium have been studied namely; O/A phase ratio, contact time, settling time, and the temperature.

INTRODUCTION

Vanadium is commercially important as a constituent for several alloys and catalysts. Nowadays, vanadium is mostly recovered as a co-product from secondary sources or from industrial waste stream such as titaniferrous magnetite, fly ash, spent catalyst and petroleum coke (Alibrane and Alike, 2008). Already in 1966, it was reported that eleven solvents in the US were used for vanadium recovery from its ores and slags (House, 1967). The solvents more frequently employed are various amines and alkyl phosphates. Alkyl phosphoric acids extract tetravalent vanadium, which was not extracted by amines. Secondary, tertiary and quaternary amines extract pentavalent vanadium at pH more than 2 (Ritcy and Ashbrook, 1979). The Vanadium Corporation of America operates a plant with a mixed solvent system

consisting of a mixture of DEHPA, heptadecyl phosphoric acid, primary alcohol and a tertiary amine in kerosene (Merrit, 1971).

As a matter of fact, both the molybdate and vanadate ions form various types of uni- and multi-nuclear oxo-complexes in aqueous solutions depending on the solution pH and the concentration of the ions. Thus, for the separation and purification of the two metals by solvent extraction, an appropriate extractant must be selected to extract and separate these ions at aqueous-phase conditions. It has been reported that these metals can be separated from hydrochloric acid solution (Komasawa et al., 1987) using tri-n-butyl phosphate, from sulfuric acid solution by bis (2-ethylhexyl) phosphoric acid and from sulfite by tri-n-octylamine at pH 2.5 (Biswas et al., 1985). In the meantime, nickel, molybdenum and

vanadium could successively be isolated from their sulfate leach liquor using a single extractant; viz, bis (2-ethyl-hexyl) monophosphoric acid (D2EHPA), through employing a suitable pH for each element. The extraction behavior of molybdenum and vanadium was varied, depending on the feed concentration of the metal and the pH value. This might arise from variation of the ionic species in the aqueous solution (Tsuboi et al., 1993). The separation factor of molybdenum and vanadium using D2EHTPA was found to be greater than in the case of D2EHPA.

On the other hand, vanadium can be extracted from its sulfate leach liquor using primene 81R and alamine336 dissolved in kerosene, where these solvents can be used to extract vanadium (V) at different acidic pH values. Thus, primene 81R allows a broad pH range for the extraction of vanadium (V), however, alamine336 was restricted to pH values less than 4 and the loading capacity of primene81R was greater than alamine336 (Lozano and Godinez, 2003). The presence of a modifier was necessary in order to avoid cruds or third phase formation.

One of the principal problems during vanadium recovery from combustion residues was its purification mainly from iron and nickel. This can be achieved by its selective solvent extraction from the liquors obtained by ash-leaching. The extraction of vanadium by amines was complicated because its prior oxidation to V^{+5} was necessary and in this case the suitable pH was between 2 and 4. using 20% of amines, and contact time 3-5 minutes, it was found that secondary amines are more effective than tertiary and quaternary and under these conditions Ni would not be extracted with vanadium but Fe would be extracted. On the other hand, DEHPA extracts V in its tetravalent state at pH 1.9 and concentration 40-60% for a contact time of 2-4 minutes, leaving almost all the initial Ni in the aqueous phase; however iron would be extracted with vanadium in low concentration (Giavarini, 1982).

A process for the recovery of vanadium

from black shales was performed using pressure acid leaching, solvent extraction and precipitation, followed by calcination to produce vanadium pentoxide. Pressure acid leaching was an efficient method for the extraction of vanadium from this material. Using optimum conditions of a reaction time of 3h, a H_2SO_4 concentration of 200 g/L, a leaching temperature of 180°C and a liquid to solid ratio of 1/2, the leaching efficiency of vanadium attained 76%. The applied solvent extraction system involved 10% D2EHPA, 5% TBP and 85% sulphonated-kerosene, an O/A ratio of 1/1, a pH of 2.3 at room temperature and the extraction yield was 98.1%. 25% H_2SO_4 was used in stripping process at O/A ratio 5/1 at room temperature, the stripping yield was 99.5% (Minting, 2009). On the other hand, a mixture of DEHPA and TBP in kerosene was used to extract vanadium from petroleum coke by means of salt roasting and acidified by dilute sulfuric acid. Vanadium should be in its tetravalent state and iron must be reduced to its bivalent state before the extraction to minimize its extraction using a temperature between 25 to 40°C, an O/A phase ratio of 3/1 and a contact time 3 to 4 minutes whereas 1.5 M sulphuric acid was used for stripping vanadium from the organic phase (Fouad and El-Rakaiby, 2009).

In the present work, the synergetic solvent mixture (DEHPA and TBP) was used for vanadium extraction from sulphate leach liquor of the black shale of Nakheil mine, NW Quseir, Egypt. After proper leaching of the working ore material with sulphuric acid, the conditions for extraction of vanadium have been optimized to minimize the co-extraction of Fe, Zn and Ni and the factor affecting the stripping of vanadium from organic phase have been optimized to get maximum re-extraction of vanadium and leaving the Mo in the organic phase.

EXPERIMENTAL

Material

A technological black shale sample weighing 50 kg was collected from the intercala-

tions of the Duwi and Dakhala shale Formations, Nakheil mine, NW Quseir, Egypt. The sample was crushed, quartered and pulverized to -1.66mm in size. Major and trace elements were analyzed by the inductive coupled plasma-mass spectrometry (ICP-MS) in ACME laboratories of Vancouver, Canada and the obtained results were shown in Table 1. From these data, the concentration of vanadium was 2422 $\mu\text{g/mL}$ where it is found dominant in the residual fraction according to the sequential extraction procedure [Fouad, Rakaiby, 2009], Zn 2341 $\mu\text{g/mL}$, Mo 569.1 $\mu\text{g/mL}$, Ni 272 $\mu\text{g/mL}$ and Fe 1.61%.

Table 1 : Chemical analysis of the major oxides(wt%) and trace elements(ppm) , in the studied black shale, Nakheil mine, Quseir area

Major Oxides	Concentration (%)	Trace elements	Concentration ($\mu\text{g/mL}$)
SiO ₂	16.92	V	2422
TiO ₂	0.21	Cu	163
Al ₂ O ₃	4.37	Zn	2314
Fe ₂ O ₃	1.61	Co	5.9
MgO	0.68	Ni	272
CaO	14.72	As	19.7
Na ₂ O	0.12	Cd	232.8
K ₂ O	0.41	Mo	569.1
P ₂ O ₅	3.38	Pb	9.3
MnO	0.02	Zr	63.6
Cr ₂ O ₃	0.08	Hf	1.6
Total C	21.81	Nb	4.4
Total S	3.20	Ta	0.3
L.O.I	32.37	Th	3.3
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Preparation of the Sulphate Leach Liquor

A sulfate leach liquor was prepared using the previously optimized leaching conditions (Fouad and El-Rakaiby, 2009) using 250 ml 6M sulfuric acid for 50 gm of ore ground to a grain size of 0.2 mm and an agitation time for six hours at 90°C. The obtained slurry was then filtered and washed with hot water and made up to volume in 250 ml volumetric flask. The leaching efficiency of vanadium was 98%. The latter and the other trace elements that might interfere in the extraction i.e Mo, Ni,

Zn, and Fe were analyzed in the obtained leach liquor and their concentrations were found to attain 480 $\mu\text{g/mL}$, 100 $\mu\text{g/mL}$, 50 $\mu\text{g/mL}$, and 0.3 % respectively. In this analysis, the atomic absorption spectrometer model Unicam 969 supplied with acetylene and nitrous oxide burner heads was used.

Extraction Procedure of Vanadium Using DEHPA/TBP

A mixture of DEHPA/TBP was used to extract V from the sulfate leach liquor prepared from black shale of Nakheil mine. The solvent TBP was essentially added as a diluent modifier to improve phase separation. Iron powder has indeed been added to the leach liquor to reduce Fe⁺³ to Fe⁺² in order to decrease the extraction of Fe with V and to reduce all V to V (IV). However, the amount of the added iron powder depends on the iron concentration in the leach liquor. Its oxidation potential is between 250 and 300 mV. The relevant factors affecting maximum extraction of V were carried out using 50 ml of the prepared sample solution and to which 0.25 gm of iron powder was added. After ten minutes, the solution was filtered and then its pH was adjusted at 0.8 by ammonia followed by adding 100 ml of mixed DEHPA/TBP in kerosene. Extraction was then followed using a mixed solvent concentration of 50% (in a ratio of DEHPA/TBP of 2/1.5) and a shaking time 15 minutes, settling time 5minutes at room temperature then the aqueous phase was separated for analysis of V, Mo, Zn, Ni and Fe. Choice of pH 0.8 was due to the fact that preliminary experiment indicated that at this pH value, both Zn and Ni were not extracted while that of iron was relatively low extracted. The studied principal extraction factors that affect the V extraction by DEHPA/TBP have indeed included; the pH of leach liquor, DEHPA / TBP ratio, solvent concentration, an O/A ratio, contact time, settling time, concentrations of V in leach liquor, the iron powder concentration besides the reducing time for Fe³⁺, as well as the extraction temperature and the number of extraction cycles.

RESULTS AND DISCUSSION

Optimization of V Extraction Conditions

Effect of pH

The effect of the leach liquor pH on the extraction of vanadium versus the associated elements using DEHPA/TBP was studied in the range from 0.5 to 1.5 using ammonia solution for pH adjustment while the other factors were kept constant. The obtained data shown in Table (2) indicated that by increasing the pH, the V and Mo extraction increases as well as the other elements, however in varying degrees. Thus at pH1, the extraction of Zn, Ni and Fe increased, to 10, 30 and 15.3 % respectively and therefore, the optimum pH would be 0.8 at which the extraction efficiency of V and Mo attained up to 80.6 and 90% respectively while almost no extraction for Zn and Ni together was observed while only 4.5 % Fe were extracted. Both the molybdate and vanadate ions form various types of uni-and multi-nuclear oxo-complexes in aqueous solutions depending on the solution pH and the concentration of the ions. Thus, for the separation and purification of the two metals by solvent extraction, an appropriate extractant must be selected to extract and separate these ions at aqueous phase conditions (Komasawa et al., 1987).

Table 2: Effect of pH on the extraction efficiency of V and the associated elements

pH	V %	Mo %	Zn %	Ni %	Fe %
0.5	50.3	80	-	-	3
0.8	80.6	90	-	-	4.5
1	86.6	90	10	30	15.3
1.5	90	90	25	60	20.7

(-): denotes under detection limit

Effect of DEHPA/TBP ratio

The effect of DEHPA/TBP ratio on the extraction efficiency of V was studied from 2/0.5 to 0.5/2 respectively while the other factors were kept constant. From the data shown in Table (3), it was clear that Zn, Ni and Fe extraction increased when the concentration of

TBP increased since the latter has been added to the organic phase as a diluent to improve the phase separation characteristics [Alibrice M., et al, 2008]. On the other hand, as the concentration of DEHPA decreased V and Mo extraction decreased when the concentration of DEHPA decreased. Accordingly, it was clear that a ratio of DEHPA/TBP of 2/1.5 was the optimum ratio for vanadium 80% while molybdenum 90% extraction.

Table 3: Effect of DEHPA/TBP ratio on the extraction efficiency of V and the associated elements

DEHPA/TPB	V %	Mo %	Zn %	Ni %	Fe %
2/0.5	44.8	92	-	-	4
2/1	70.3	93.5	-	-	4.5
2/1.5	80	90	-	-	4.5
1/2	60.3	90	16.8	22.4	10.7
0.5/2	24.8	77.8	23.2	36.8	15.3

Effect of DEHPA/TPB concentration

The effect of DEHPA/TBP concentration in kerosene on V extraction was studied in the value range of 30 to 70% while all the other experimental conditions were kept constant. From the data presented in Table (4), it was obvious that V and Mo extraction efficiency was directly proportional with the concentration of solvent to reach 80.6% for V and 90% for Mo at 50% concentration of the solvent in kerosene and then it became constant. Under these conditions neither Zn nor Ni has been extracted while Fe extraction was only 4.5%, where the pH value of the leach liquor (equals to 1) was optimum for Mo and V but not for Ni and Zn as studied before.

Table 4: Effect of solvent concentration on the extraction efficiency of V and the associated elements

Solvent concentration (%)	V %	Mo %	Zn %	Ni %	Fe %
30	33.3	80.7	-	-	5
40	58.2	85	-	-	4.5
50	80.6	90	-	-	4.5
60	80.6	90.6	10.9	-	3.8
70	80	92	15.8	-	3.8

Effect of organic / aqueous phase ratio

The effect of the organic to aqueous phase ratio on vanadium extraction was studied in the range from 1/3 to 3/1 while and the other factors were kept fixed. The obtained data shown in Table (5) indicate that extraction of V, Mo and Fe increases with increasing the organic/aqueous phase ratio to reach 80.6%, 90% and only 4.5% for V, Mo and Fe respectively at organic to aqueous ratio of 2/1. Under these conditions, Ni extraction was almost nil (below its detection limit < 0.01 ppm) while Zn was extracted to only 5% level.

Table 5: Effect of organic / aqueous phase ratio on the extraction efficiency of V and the associated elements

O/A	V %	Mo %	Zn %	Ni %	Fe %
1/3	31.7	72	-	-	3
1/2	48.9	80	-	-	3
1/1	67.8	90	-	-	3.6
2/1	80.6	90	5	-	4.5
3/1	80.6	95	20	-	4.5

Effect of iron powder concentration on the reduction of Fe and V

The Effect of iron powder concentration on the extraction of V and Fe was studied by adding 0.05 to 0.5 gm to 50 ml of leach liquor while the other factors were fixed at the same conditions. From the data shown in Table (6), it was clear that the extraction efficiency of vanadium increased while that of Fe decreased by increasing the iron powder concentration but that of Mo has not changed. The iron powder added to the leach liquor would decrease Fe extraction while increasing vanadium extraction through reduction of iron to Fe^{+2} and of vanadium to V(IV). This was because Fe^{+3} would be extracted with DEHPA and its distribution factor was higher than that of V (IV) while the Fe^{2+} extraction with DEHPA/TPB was very low. So the optimum iron powder quantity of 0.25g would be adequate to reduce the associated Fe in the working leach liquor (5 g/l) and the oxidation potential of the working leach liquor should be between 250 – 300 mV.

Table 6: Effect of iron powder on the extraction efficiency of V, Fe and the associated elements

Added Fe powder (g)	V %	Mo %	Zn %	Ni %	Fe %
0.05	67.4	85.6	5	-	48.6
0.125	72.8	87.5	5	-	25.7
0.25	80.6	90	3.5	-	4.5
0.5	80.6	90	3.4	-	4.5

Effect of reduction time on V extraction

The effect of the reducing time on the extraction efficiency of Fe and V was studied by adding 0.25 g of iron powder to 50 ml of the working sulphate leach liquor and allowing a reduction time ranging from 5 to 20 minutes before filtration and adjusting the pH to 0.8. In these experiments, solvent concentration was 50% at an O/A ratio of 2/1 and the DEHPA/TBP ratio was 2/1.5. The obtained data shown in Table (7) indicated that Fe extraction decreased with the increase of reduction time and became constant after 10 minutes, since most of Fe (III) was reduced to Fe (II) while that of V decreased after 10 minutes. On the other hand, Mo extraction was constant from 5 minutes till 20 minutes (90%), hence the optimum contact time used was ten minutes.

Table 7: Effect of reducing time on the extraction efficiency of V and the associated elements

Reduction time (min.)	Fe %	Ni %	Zn %	Mo %	V %
5	20	-	-	90	80.5
10	5	-	3	90	80.5
20	5	-	3	90	70

Effect of temperature

The effect of temperature on the extraction of vanadium was studied in the range from room temperature till 60°C and the other factors were kept fixed. The obtained data shown in Table (8) indicated that the best extraction efficiency for V and Mo was at room temperature and when it increased, the extraction of

vanadium and molybdenum decreased and this may be due to that at elevated temperature the solvent partially dissociates thus its extraction efficiency for V and Mo decreases.

Table 8: Effect of temperature on the extraction efficiency of V and the associated elements

Temperature (°C)	Fe %	Ni %	Zn %	Mo %	V %
Room temp.	5	-	3	90	80.5
40°C	12.4	-	8.7	90	75.8
60°C	30	11.4	14.6	75.5	57

Effect of contact time

The effect of contact time on vanadium extraction from the working sulphate leach liquor of Nakheil mine black shale was studied from 5 to 20 minutes while the other factors were kept fixed. The obtained results were shown in Table (9) where it was clear that as the contact time increased the extraction of V increased till 80% at a contact time of 15 minutes and remained constant thereafter where the solvent becomes saturated. Iron extraction has however decreased as the contact time increased while Mo extraction was constant with contact time.

Table 9: Effect of contact time on the extraction efficiency of V and the associated elements

Contact time (min.)	Fe %	Ni %	Zn %	Mo %	V %
5	17.4	-	-	92	35
10	10.3	-	3	90	60
15	5	-	3	90	80
20	5	10.5	5.7	90	80

Effect of settling time

The effect of the settling time of the two phases after their mixing upon the extraction of V from the working sulphate leach liquor was studied from 2 to 7 minutes while the other factors were kept fixed. The obtained results shown in Table (10) clearly revealed that the extraction of V increased to 80 % when using 5 minutes as the settling time then it decreased thereafter, while that of Fe increased beyond a settling time of 5 minutes while that of Mo has not been changed.

Table 10: Effect of settling time on the extraction efficiency of V and the associated elements

Settling time (min.)	Fe %	Ni %	Zn %	Mo %	V %
2	4	-	-	92	60.4
5	5	-	3	92	80
7	10	-	3	95	70.8

Effect of V concentration

The effect of vanadium concentration on its extraction efficiency was studied by using three sulphate sample solutions namely; a diluted sample (240 µg/mL), a normal leaching sample (480 µg/mL) and a third sample has been leached after heating the sample at 600°C for 2 hours to get rid of the organic carbon hence increasing the concentration metals found, and was then subjected to sulphuric acid leaching under the same conditions. The vanadium concentration after filtration, washing and completing to 250ml volumetric flask was found to assay 750 ppm and that of iron 2.2 %. Before extraction, 0.25g Fe was added to 50 ml of each sample which was then left for 10 minutes before filtering and adjusting the pH to 0.8. The concentration of the used solvent was 50%, DEHPA/TPB in a ratio of 2/1.5, O/A ratio of 2/1 and using a contact time of 15 minutes and a settling time of 5 minutes. The obtained data shown in Table (11) reveal that as the V concentration increased, its extraction efficiency increased but at the high concentration of V (750 µg/mL) the extraction of other elements increased to reach (40, 20, 45 %) for Zn, Ni and Fe respectively, while Mo extraction remained almost constant (90-95 %). Therefore the optimum condition for extraction of vanadium would be 480 µg/mL.

Table 11: Effect of vanadium concentrations on their extraction efficiencies and the associated elements

V conc. (µg/mL)	Fe %	Ni %	Zn %	Mo %	V %
240 µg/mL	-	-	-	90	40
480 µg/mL	5	-	3	92	80
750 µg/mL	45	20	40	95	85

Effect of the number of the extraction cycles

The number of cycles upon the extraction of vanadium was studied in the range of 1 to 4 cycles. The fixed conditions involved adding 0.25 g iron powder which was left for 10 minutes before filtration followed by adjusting the pH at 0.8 and the concentration of solvent was 50% (DEHPA/TBP ratio 2/1.5), at the O/A phase ratio of 2/1 for a contact time of 15 minutes and a settling a time of 5 minutes. After separating the organic phase, another equal volume of fresh organic solvent was mixed with the same aqueous phase at the same conditions then separating the organic phase and this treatment was repeated twice at the same conditions. After those four cycles, V, Zn, Ni, Mo and Fe in the aqueous phase were analyzed and the obtained data shown in Table (12) indicated that vanadium extraction needs two cycles to reach 92% extraction efficiency. At the third cycle the extraction of Zn, Ni and Fe increased progressively and therefore two cycles would be optimum for 92% vanadium and 93 % for molybdenum extraction in order not to increase the extraction efficiencies of the associated elements.

Table 12: Effect of the number of extraction cycles on the extraction efficiencies of V and the associated elements

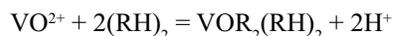
No. of cycles	Fe %	Ni %	Zn %	Mo %	V %
1	4.5	-	-	92	80
2	4.5	-	3	93	92
3	10	12.3	18.6	97.6	96
4	26.8	24.8	30.6	97.8	96

It can be concluded that after studying the factors that affect the extraction of V using a mixed solvent of DEHPA and TBP in kerosene, the best conditions for extraction of vanadium is 50% (DEHPA/TBP with ratio 2/1.5), an O/A phase ratio of 2/1, a contact time of 15 minutes, a settling time of 5 minutes at pH 0.8. Iron powder must be added to decrease the extraction of iron and increase that of V besides two cycles for extraction. Under these conditions, the vanadium and molybdenum

extraction efficiencies were 92 % and 93 % respectively. Therefore, separation of both elements would be undertaken during a selective stripping process.

Optimization of Vanadium and Molybdenum Stripping Conditions

After vanadium and molybdenum extraction from the working sulphate leach liquor of Nakheil mine black shale sample into the studied organic phase (DEHPA/TBP), it was necessary to study the relevant stripping factors to achieve their separation and recovery. For this purpose, an adequate quantity of the loaded organic phase was prepared using the optimum extraction conditions to study the possibility of their selective separation. The concentration of both V and Mo in the prepared loading organic phase attained was 442 µg/mL and 93 µg/mL respectively. The relevant studied factors that would affect the possible selective Mo/V stripping involved the type of the stripping solution, the organic to aqueous phase ratio, the effect of temperature, the contact time, settling time and the number of stripping cycles. In the working solvent mixture DEHPA and TPB (TBP was added as diluent modifier to improve the phase separation) vanadium was extracted in its cationic form. The following equation can represent its extraction mechanism (Hirai et al., 1995).



Type of stripping solution

Several experiments were performed using different stripping solutions to study the stripping of V and Mo from the loaded organic phase namely; H₂O, H₂SO₄ and sodium carbonate [Baldwin, et al, 1974] with different concentrations. In these experiments the O/A ratio was (1/1) for a contact time of 10 minutes followed by a settling time of 5 minutes after which the aqueous phase was separated and subjected to analysis of V and Mo as shown in Table (13). From these results, it was clear that sodium carbonate (100g/L) gives the best results for vanadium stripping while most of Mo remained in the organic phase.

Table 13: Effect of the type of the stripping solution on V/Mo stripping of vanadium

Strip solution	Mo stripping (%)	V stripping (%)
H ₂ O	-	5
H ₂ SO ₄ (1.5M)	5.4	10.5
H ₂ SO ₄ (3M)	5.4	20.7
Na ₂ CO ₃ (50g/l)	9.5	30
Na ₂ CO ₃ (100g/l)	8.7	50

Effect of O/A phase ratio

The effect of different O/A phase ratios (1/3, 1/2, 1/1, 2/1 and 3/1) were studied on V/Mo stripping from organic phase and the obtained data were represented in Table (14). In these experiments 100g/L Na₂CO₃ was used for a contact time of 10 minutes and a settling time of 5 minutes. From these results, it was clear that the vanadium stripping increased to reach up to 85.5 % at the O/A phase ratio of 2/1 and remained constant afterwards while Mo stripping decreased to reach 4.2% only at the same O/A phase ratio (2/1).

Table 14: Effect of O/A phase ratio on V/Mo stripping

O/A	Mo stripping (%)	V stripping (%)
1/3	23	33.6
1/2	21.6	56
1/1	4.5	77.9
2/1	4.2	85.5
3/1	4	85.5

Effect of temperature

The effect of temperature on stripping V/Mo from the working loaded organic solvent using 100g/l Na₂CO₃ solution was studied from room temperature to 80°C, while the other factors were fixed at an O/A ratio of 2/1 for a contact time of 10 minutes and a settling time of 5 minutes. From the obtained data, (Table 15), it was clear that increasing the stripping temperature has an adverse effect upon V stripping and therefore the room temperature has been used for its stripping (85.5 %) while that of Mo remained 4.2 % only.

Table 15: Effect of temperature on V/Mo stripping

Temperature (°C)	Mo stripping (%)	V stripping (%)
Room Temp.	4.2	85.5
40	5.6	80.2
60	5.6	72.6
80	5.6	45

Effect of Contact time

The effect of contact time on vanadium selective stripping from the working loaded organic phase was studied in the range from 5 to 20 minutes while the other factors were fixed at an O/A ratio of 2/1, a settling time of 5 minutes and using 100g/l Na₂CO₃ at room temperature. From the obtained results represented in Table (16), it was clear that the stripping of V increased with contact time from 5 to 10 minutes to 85.6% then it became constant. On the other hand, stripping of Mo from the organic phase was very low (4.2% after ten minutes) and did not change thereafter.

Table 16: Effect of contact time on V/Mo stripping

Contact time (minutes)	Mo stripping (%)	V stripping (%)
5	3.3	55.5
10	4.2	85.65
15	4.3	85
20	4.3	85

Effect of settling time

The effect of settling time on the selective stripping of V from the working organic phase was studied from 2 to 7 minutes at an O/A phase ratio of 2/1 for a contact time of 10 minutes using 100g/l Na₂CO₃ at room temperature. From the data shown in Table (17), it was clear that vanadium stripping increased to 85.6%, associated with only 4.3 % Mo stripping as the settling time increased to 5 minutes and remained constant thereafter.

Table 17: Effect of settling time on V/Mo stripping

Settling time	Mo stripping (%)	V stripping (%)
2	5	60
5	4.3	85.6
7	4.3	85.6

Effect of the number of stripping cycles

The number of stripping cycles of vanadium versus molybdenum from the working loaded organic phase was studied at fixed conditions of 100g/l Na₂CO₃, O/A phase ratio 2/1, shaking time 10 minutes and settling time 5 minutes. This was followed by separating the aqueous phase, adding another volume of fresh aqueous stripping reagent to the same organic phase at the same conditions and this was repeated once more. From the data shown in Table (18), it was found that vanadium needed 2 cycles for 96% stripping from the organic phase. Under these conditions Mo co-stripping would not exceed 4.3%.

Table 18: Effect of the number of cycles on V/Mo stripping

No. of cycles	Mo stripping (%)	V stripping (%)
1	4.3	85.6
2	4.3	96
3	5	97

CONCLUSIONS

The relevant factors for extraction of vanadium from the sulphate leach liquor of black shale from NW Quseir have been optimized using the synergistic mixture of DEHPA/TBP in kerosene after proper reduction of the working leach liquor using 5 gm/l iron powder. The optimum factors were found to involve a pH 0.8, 50% synergistic solvent concentration at DEHPA/TBP ratio of 2/1.5, O/A phase ratio 2/1, contact time 15 minutes followed by settling time 5 minutes at room temperature. At these conditions it was found that two extrac-

tion cycles are efficient to recover 92% vanadium.

Selective stripping of 96% vanadium was achieved using 100 g/l Na₂CO₃ solution for two cycles at an O/A ratio 2/1, contact time 10 minutes and settling time 5 minutes at room temperature, where Mo was left in the organic phase. Further studies will be done for the stripping of molybdenum from the organic phase.

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استخلاص الفاناديوم بواسطة خليط من ثنائي إيثايل هيكسيل حمض الفوسفوريك و ثلاثي بيوتيل الفوسفات من الطفلة السوداء الرسوبية من منطقة القصير، البحر الأحمر، مصر

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لقد تم دراسة إستخلاص الفاناديوم من محلول الإذابة بالكبريتيك للطفلة السوداء المستخرجة من منجم النخيل الواقع شمال غرب القصير، البحر الأحمر، بجمهورية مصر العربية بواسطة خليط من مستخلصين عضويين هما ثنائي إيثايل هيكسيل حمض الفوسفوريك و ثلاثي بيوتيل الفوسفات المذابان في الكيروسين. لقد تم تجميع عينة تكنولوجية لهذه الدراسة من الطفلة السوداء ووجد أنها تحتوى على ٢٤٠٠ جزء في المليون من الفاناديوم، ٢٣٠٠ جزء في المليون من الزنك، ٥٧٠ جزء في المليون من المولبدينوم، ١,٦٪ حديد و ٢٧٢ جزء في المليون من النيكل. لقد وجد أن بإضافة بودة الحديد تقلل من إستخراج الحديد من المحلول و ذلك من خلال ضبط الأس الهيدروجيني للمحلول المذاب عند ٠,٨ و ذلك لتقليل إستخلاص عنصرى الزنك والنيكل المصاحبين للفاناديوم في المحلول. لقد تم دراسة بعض العوامل لإستخلاص أعلى تركيز من الفاناديوم و هم نسبة المستخلص العضوى (ثنائي إيثايل هيكسيل حمض الفوسفوريك إلى ثلاثي بيوتيل الفوسفات)، تركيز المذيب، نسبة الطور العضوى إلى الطور المائى، وقت التلاحم، وقت الفصل، درجة الحرارة، كمية مادة الإختزال بجانب وقت الإختزال. إن تقنية إسترجاع عنصر الفاناديوم تم بواسطة ١٠ جرام/لتر من محلول كربونات الصوديوم تاركا المولبدينوم في الطور العضوى. لقد تم دراسة بعض العوامل المؤثرة لإسترجاع عنصر الفاناديوم و هم نسبة الطور العضوى إلى الطور المائى، وقت التلاحم، وقت الفصل و درجة الحرارة.