

Alkaline selective leaching of uranium from carbonate-rich black shale wadi naseib, southwestern sinai, Egypt

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ABSTRACT

A technological sample assaying 1600 ppm U and about 2.8% CuO in a carbonate-rich black shale host rock has been collected from Wadi Naseib area of Southwestern Sinai. The XRD analysis has revealed that the predominating carbonate mineral is ankerite which the clay minerals are found to be represented by kaolinite, montmorillonite and illite. Due to the mineralogy of the working ore material, it was necessary to apply carbonate leaching for selective leaching of uranium. This is due to the fact that acid leaching is not suitable due to the present of high carbonate content besides avoiding the co-leaching of the present copper values. After studying the relevant alkaline leaching factors for dissolving about 97% of uranium from the studied working sample are 50 g/l Na₂CO₃ and 20 g/l NaHCO₃, S/ L ratio 1/3, agitation time 1.5h at room temperature.

Uranium was recovered from the carbonate leach liquor through the anionic exchange resin Lewatite Monoplus M 500 and from the eluate, uranium was precipitated by sodic decomposition to obtain Na₂U₂O₇ product. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Egyptian black shale;
Alkaline leaching;
Uranium.

INTRODUCTION

The studied ore material sample was collected from Wadi Naseib area which is located in SW Sinai between long. 33° 25' and 33° 26' E and lat. 29° 02' and 29° 04' N.

The host rock of the studied mineralization is the high-carbonate black shale (oil shale) of the lower member of the early Carboniferous Um Bogma Formation. Due to its high carbonate content which would result in excessive acid consumption, besides avoiding simultaneous leaching of the copper values, alkaline leaching was achieved for selective uranium leaching. For this purpose, a representative technological sample has been collected and pre-

pared for chemical analysis by XRF and another sample portion was subjected to XRD for mineralogical study.

Alkali carbonate (sodium or less commonly ammonium) is generally used for uranium leaching from its ores that are high in carbonate gangue minerals like calcite, dolomite, etc. This depends on the fact that the carbonate anion forms with uranium stable soluble uranyl carbonate complex $[\text{UO}_2(\text{CO}_3)_n]^{2-2n}$ [1].

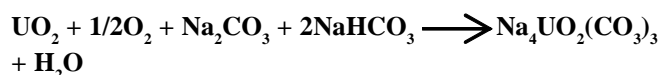
The alkali leaching can be applied to both primary and secondary mineral deposits, however after oxidation of the former. Several studies of the alkali carbonate leaching have been achieved including the use of f^{2-5} and from which several important

advantages over acid leaching have been indicated, namely its selectivity where comparatively pure solutions are readily obtained besides its non-corrosive nature. Also, the consumption of the reagent by the ore is low and uranium can be readily recovered from the leach liquor. Finally, the carbonate solutions can be regenerated for further leaching cycles. However, there are some limitations to the use of carbonate leaching due to its mild nature so that some uranium minerals are not solubilized by carbonate leach solutions. However, alkali leaching requires fairly fine grinding of the ore in order to obtain reasonable reactions rates. Alternatively, carbonate leaching could be performed under relatively high pressure and temperature in suitable autoclaves.

The carbonate reaction with U^{6+} can indeed be represented by the following reaction:

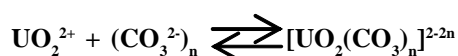


The sodium hydroxide resulting in the above reaction would increase the solution pH, a matter which would lead to uranium precipitation. To avoid the latter, sodium bicarbonate is used to buffer the hydroxide formed^[4] and the overall reaction can thus be represented as follows:



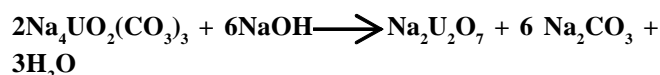
Finally, it might be interesting to mention that presence of sulfide (e.g. pyrite) or sulfate minerals (e.g. gypsum) is harmful for carbonate leaching where high consumption of the relatively expensive sodium ion would occur. According to^[6-8], the sulfide content should not exceed 0.4 - 0.5% equivalent sulfur.

^[1], studied probably the presence of complex uranyl carbonate ions $[UO_2(CO_3)_n]^{2-2n}$ in carbonate solution and it is believed that the ionic species are governed by the following equilibrium reaction although the underlying processes are indicated as follows:



From the carbonate solution uranium can be recovered in several ways including sodic decomposition when the product would be sodium diuranate ($Na_2U_2O_7$). The filtrate from this precipitation would

be then recarbonated with carbon dioxide for reuse in leaching more ore. Alternatively, the carbonate solution could be acidified with hydrochloric acid and boiled to remove carbon dioxide, with uranium precipitated as the hydroxide by adjusting the pH to neutrality.



In addition, the anionic uranium complex can be recovered through an anionic exchange and from the obtained eluate, the uranium may be precipitated with an alkaline reagent, such as ammonia, or sodium hydroxide, or else with hydrogen peroxide^[9-11].

MATERIALS AND METHODS

Materials

A representative sample portion of the study high-carbonate carbonaceous black shale that was collected from W. Naseib area of SW Sinai was properly ground and subjected to complete chemical analysis of its major oxide constituents besides some trace elements using the XRF technique. Prior to the latter, an X-ray diffraction of the representative sample was also achieved to define its mineralogical composition.

Exchangers

For the experiments the polystyrene-DVB-based anion exchanger Lewatit Monoplus M 500 contains quaternary amine groups, it is practically mono-functional and characterized by high basicity and high stability. Ionic form as shipped Cl^- , Matrix is crosslinked polystyrene, Structure: gel type beads, Appearance: yellow translucent. Total capacity: 1.3meq/ml, Stability at pH range 0-14^[12,13].

Experimental procedures

Uranium leaching procedure

Several uranium leaching experiments have been achieved upon the studied high-carbonate carbonaceous black shale by stirring different sample leaching in the working alkali leach solution under different conditions. The purpose was to determine the optimum values of the relevant leaching factors. These involved the effect of the alkali carbonate

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concentration, the S/L ratio, the contact time and the temperature besides the effect of adding sodium bicarbonate. In these experiments and except otherwise cited, 5 g of the studied working sample was used.

Ion exchange recovery of uranium

For the IX recovery of uranium from the study carbonaceous black shale, a proper solution was prepared thereof using the determined optimized leaching factors. For this purpose, the Lewatit Monoplus M 500 anion exchange resin was used by packing 10 ml wsr in a glass column of 1.5 cm diameter. After uranium loading, it was eluted using 1M sodium chloride solution acidified with 0.15N H_2SO_4 and from the obtained eluate, uranium was precipitated as a sodium diuranate product via sodic decomposition.

Analytical procedures

Bulk analysis of the working sample

Another representative sample of the working ore material was analyzed to determine both the major oxide components and some trace elements using XRF technique, then the former were achieved in the National Research Center (NRC) using Axios Advanced, Panalytical, Holland while the trace elements, were analyzed using the Nuclear Materials Authority (NMA) Philips X Unique-II spectrometer which is fitted with automatic sample changer, PW 1510 (30 positions) of Holland. For the mineralogical analysis an XRD analysis was made using the Phillips X-ray (PW3710) of NMA and which is fit-

ted with a generator (PW 1830) and Cu target tube (PW 223/20) and was operated at 40 KV and 30 mA. Finally, the precipitated sodium diuranate product was analyzed in the Chemical Warfare Main Labs by EDAX of EWAR Model FEI Inspect S, Holland.

Control analysis

For uranium analysis in the different stream solutions of the different working experiments was spectrophotometrically determined by the Arsenazo III complex^[14] using a Perkin Elmer Spectrophotometer model.

RESULTS AND DISCUSSION

Characteristics of the Working Sample

Ore sample mineralogy

The XRD analysis of the studied sample has indicated that ankerite $(Ca, Mg, Fe)(CO_3)$ is the main carbonate mineral constituent while the clay content is represented by the three principal clay minerals, viz, kaolinite, montmorillonite and illite Figure 1. In the meantime, the other mineral constituents involve quartz, gypsum besides hematite minerals.

Chemical composition

As previously mentioned, the working sample of the study carbonate-rich black shale sample has completely been analyzed by the relevant methods for both the major constituents as well as for some interesting trace elements. From the obtained results

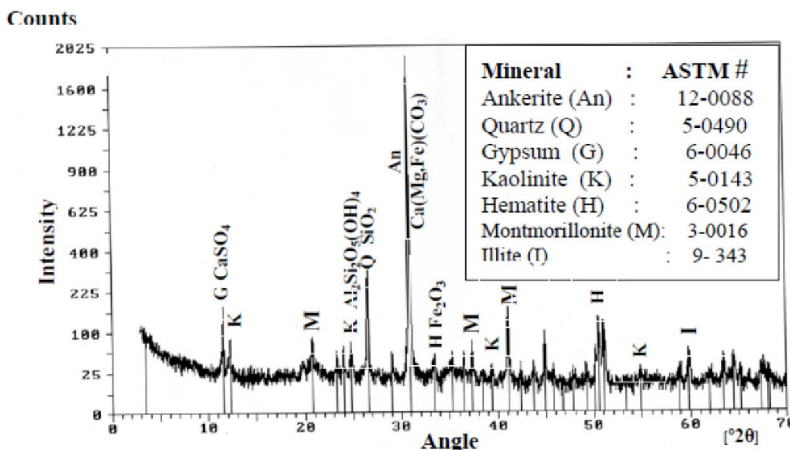


Figure 1 : XRD pattern of the working carbonate-rich black shale sample of wadi naseib area

TABLE 1 : The chemical analysis of the working sample by XRF in NRC

Component	Wt. %	Component	Wt. %
SiO ₂	15.60	K ₂ O	0.94
Al ₂ O ₃	8.00	TiO ₂	0.83
Fe ₂ O ₃	10.00	P ₂ O ₅	0.05
MgO	5.40	SO ₃	3.05
MnO	1.40	Cl	0.04
CaO	19.70	CuO	2.80
Na ₂ O	0.05	L.O.I*	30.00
Total		97.86	

* L.O.I: Total Loss of Ignition at 1000 °C

TABLE 2 : XRF analytical results of the trace elements of the working sample

Trace elements	Wt. %	Trace elements	Wt. %
Cr ₂ O ₃	0.041	SrO	0.023
Co ₃ O ₄	0.153	V ₂ O ₅	0.122
NiO	0.114	Y ₂ O ₃	0.025
ZnO	0.029	*U	0.160
ZrO ₂	0.070		

*U as element (chemically analyzed).

shown in TABLE (1 and 2), it is noticed that the main components include about 25% (CaO+MgO) together with about and 15.6% SiO₂ and 8% Al₂O₃ respectively. In the meanfine an iron content equivalent to about 10% Fe₂O₃ besides 1.4% MnO and 0.049% and 3.05% SO₃. Among the major oxides, it was revealed that copper assays up to about 2.8%.

Concerning the trace element, it was found that the interesting metal values present include mainly V and Y attaining 1220 and 250 ppm as V₂O₅ and Y₂O₃ respectively. Co and Ni are present it the extent of 1530 and 1140 ppm as Co₃O₄ and NiO respectively while uranium assays 1600 ppm.

Optimization of uranium alkaline leaching factors

Effect of sodium carbonate concentration

In order to have an estimation of the required input carbonate reagent for uranium leaching, a series of experiments was first performed.

In these experiments 5 g ore material samples (-200 mesh size) were subjected to alkaline leaching using different concentrations of Na₂CO₃ ranging from 30 to 55 g/l. The other leaching parameters were fixed at S/L ratio of 1/3 for 0.5 h agitation time at room temperature. The results are shown in Figure (2).

From the obtained results shown in Figure (2), it was found that the uranium leaching efficiency has increased by increasing the input carbonate concentrations from only 27 to 62% at 30 and 50 g/l Na₂CO₃ respectively. Further increase in the carbonate concentration to 55 g/l has an adverse effect on U leaching efficiency which was decreased to 58%. This decrease is most probably due to the generation of more OH⁻ during leaching, a matter which would result in rising in the pH to a point where diuranate would precipitate. Therefore, a 50 g/l concentration of Na₂CO₃ was thus considered as the optimum value thereof.

Effect of S/L ratio

The effect of S/L ratio upon the alkaline carbonate efficiency leaching of uranium from the studied carbonate-rich black shale ore material was studied upon in the range from 1/1 to 1/4 at the other variables were fixed at 50 g/l concentration of sodium carbonate, an agitation time for 0.5 h at room temperature and using 5 g sample portions. All results plotted in Figure (3).

From these obtained results shown in Figure (3), it is clearly evident that the best S/L ratio for leaching 62% of uranium from the studied working sample

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is 1/3 and where by increasing this ratio to 1/4 the leaching efficiency decreased to 57% this is again most probably due to the NaOH formed by increasing the S/L ratio to 1/4 is a matter which pH increased and led to partial uranium precipitation.

Effect of agitation time

Another series of experiments was performed to determine the optimum content time that would be required to obtain the best possible leaching uranium efficiency from the studied working sample. Thus, different agitation times periods varying from 0.5 to 2.5 h at the other fixed variables of 50 g/l sodium carbonate, S/L ratio of 1/3 at room temperature.

From the obtained data plotted in Figure (4), the maximum obtained leaching efficiency of 77.7% has been realized at 1.5 h. Further, increase in the agitation time to 2 and 2.5 hrs has not improved the leaching efficiency thereafter.

Effect of leaching temperature

The effect of the alkali leaching temperature was studied in the range of 50 to 100°C which the other leaching factors were fixed at a S/L ratio of 1/3 for 1.5 h and using of 50 g/l Na₂CO₃ concentration of the leach liquor. The results shown in Figure (5) reveal that increasing the leach temperature has brought an adverse effect where in the studied range, the uranium leaching efficiency has decreased down to 66% at 50°C and to 59% thereafter. This is most probably due to the increased reaction which would increase in turn the NaOH formation and which would result in uranium precipitation.

Effect of sodium bicarbonate addition

Addition of sodium bicarbonate to the alkali carbonate leaching reagent on leaching uranium from the study ore material has actually been quite necessary to neutralize the formed sodium hydroxide. Accordingly, a series of leaching experiments was performed in which sodium bicarbonate was added to the 50 g/l sodium carbonate solution in a weight ratio of Na₂CO₃/NaHCO₃ of 20/1 up to 2.5/1 i.e. in contentions ranging from 2.5 up to 20 g/l. The other fixed leaching conditions involved a S/L ratio of 1/3 at 25 °C for 1.5 h contact time.

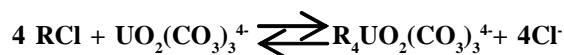
From the obtained results plotted in Figure (6), the leaching efficiency of uranium has actually increased by NaHCO₃ addition. Thus, by decreasing the weight ratio of Na₂CO₃/NaHCO₃ concentration from 20/1 to 2.5/1, the corresponding leaching efficiencies have increased from 81 up to 97.2%. Therefore, it can be concluded that the weight ratio of Na₂CO₃/NaHCO₃ of 2.5/1 would be considered as an optimum weight ratio for about 97 % uranium leaching efficiency. This increase in U leaching efficiency is actually due to presence of NaHCO₃ which prevents the solution pH from rising by the formed NaOH to the point where diuranate would precipitate.

From the above studied leaching factors of the study black shale working sample, it can deduced that the optimum conditions for dissolving about 97% of uranium could be summarized as follows:

Alkali concentration	:	50 g/l Na ₂ CO ₃ / 20 g/l NaHCO ₃
S/ L ratio	:	1/3
Agitation time	:	1.5h
Leaching temperature	:	25°C
Grain size	:	-200 mesh size

Ion exchange recovery of uranium

Ion exchange offers the possibility of selective sorption of uranium species, especially at trace concentration. The application of the anion exchange Lewatit Monoplus M 500 resin for recovery uranium from the studied black shale ore material has thus been studied after its alkaline leaching.



For this purpose, an ore material sample weighing 500 g was alkali leached using the above studied optimum leaching factors and filtration and washing, the liquor has attained 2 L. The latter has thus been found to assay 0.39 gU/l.

Uranium loading

The prepared leach liquor was then fed to the prepared resin column (10 ml wsr) at a flowrate of 0.5 ml/min (contact time 8 min). The effluent was collected every 100 ml and its uranium content was determined the obtained results are tabulated in TABLE (3) and graphically plotted in Figure (7).

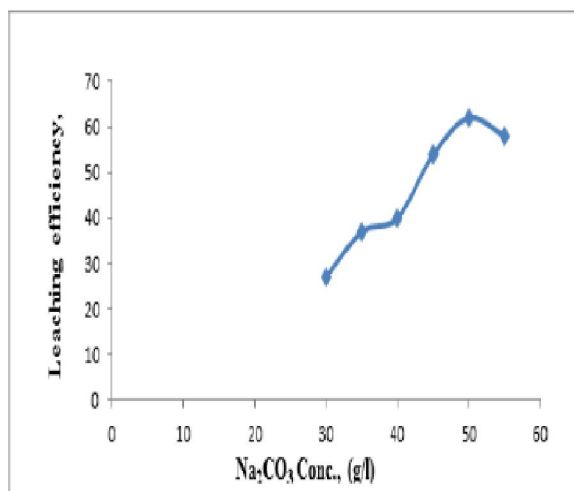


Figure 2 : Effect of sodium carbonate concentration upon uranium leaching efficiency from the studied carbonate-rich black shale ore material

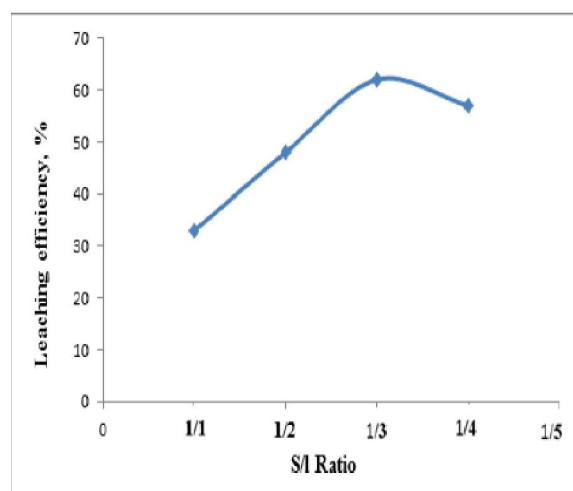


Figure 3 : Effect of S/L ratio upon uranium leaching efficiency from the studied carbonate-rich black shale ore material

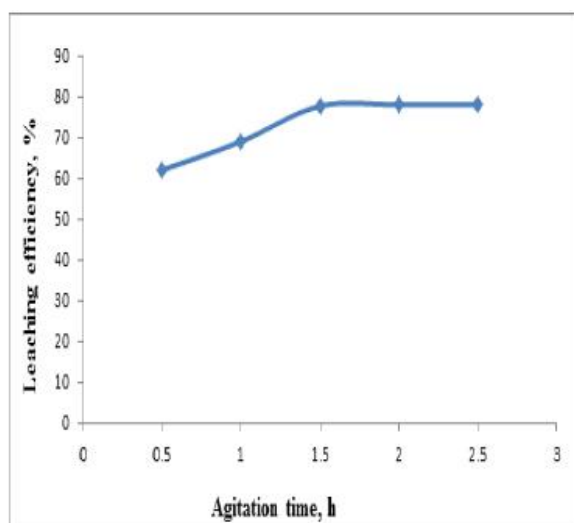


Figure 4 : Effect of agitation time upon uranium leaching efficiency from the studied carbonate-rich black shale ore Material

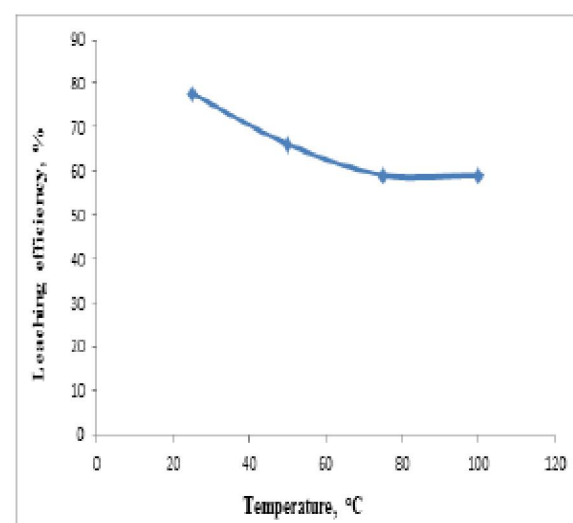


Figure 5 : Effect of temperature upon uranium leaching efficiency from the studied carbonate-rich black shale ore material

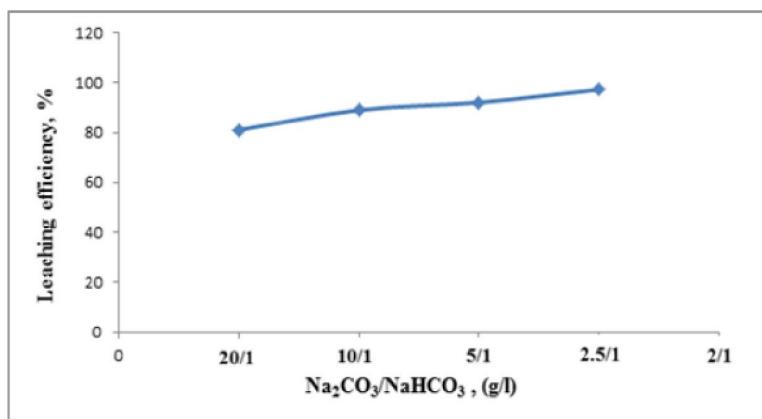


Figure 6 : Effect of sodium bicarbonate addition to 50 g/l Na₂CO₃ upon uranium leaching efficiency from the studied carbonate-rich black shale ore material

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TABLE 3 : Progressive uranium analysis in the effluent sample from the working Lewatit Monoplus M 500 resin column

Effluent sample no. (100ml)	Effluent U, conc., gl^{-1}	U adsorption efficiency, %
1-11	Nil	100
12	0.03	92.5
13	0.05	87.5
14	0.1	75
15	0.12	70
16	0.16	60
17	0.2	50
18	0.25	37.5
19	0.35	22.5
20	0.38	5

Total adsorbed U \approx 0.64 g

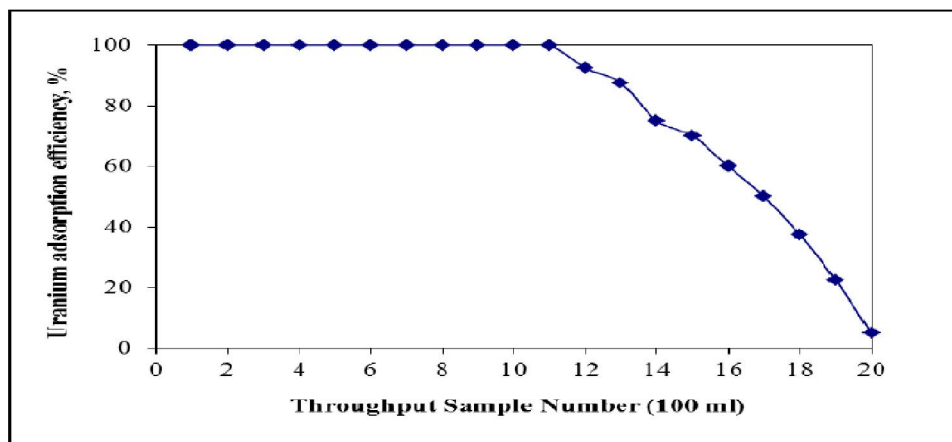


Figure 7 : Adsorption curve of uranium from the leach liquor of the working ore material upon Lewatit Monoplus M 500 resin column

Calculation of the adsorbed uranium content was found to attain 64 mg/10 ml wr. Referring to the theoretical resin capacity of 1.3 meq/ml, it would be evident that the realized adsorption efficiency has attained about 80% of the former.

Uranium elution

For uranium elution from the loaded working resin samples, the chloride elution system has been applied where 1M sodium chloride solution acidified with 0.15N H_2SO_4 was used. The eluant solution was passed through the loaded resin sample using a contact time of 8 min (flowrate of 0.5 ml/min) after a prior step up washing the working loaded resin column by distilled water. The uranium content in the obtained eluate samples (10 ml) is shown in TABLE (4) and graphically plotted in Figure (8).

From these results, it can be deduced that uranium elution attained an efficiency exceeding 95% with amaximum uranium assay of 18.19g/l in the 5th eluate sample.

Sodic decomposition

After collection the eluate samples, the contained uranium was precipitated through sodic decomposition by heating and using 10 % sodium hydroxide solution at pH of about 12. After filtration and washing, the product was calcined at 900 °C for 1 hr and obtained precipitate weighing about 0.69g of sodium diuranate would indicate that uranium has been quantitatively precipitated. The sodium diuranate analyzed by ESEM. The uranium qualitative assay is found to be about 70%. The uranium precipitation using sodic decomposition as shown in Figure (9).

TABLE 4 : Progressive uranium analysis in the eluate samples of the working loaded resin column

Eluate sample no. (10 ml)	U conc. g l^{-1}
1	2.60
2	4.20
3	5.60
4	7.10
5	18.10
6	7.30
7	5.90
8	5.10
9	3.80
10	2.90

Total eluted U \approx 0.636 g

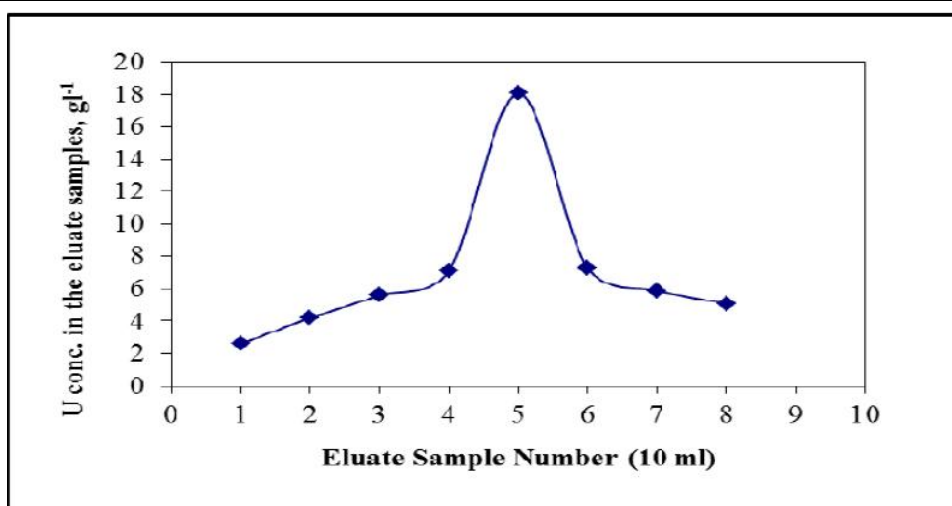


Figure 8 : Uranium elution curve from the working loaded Lewatit Monoplus M 500 resin

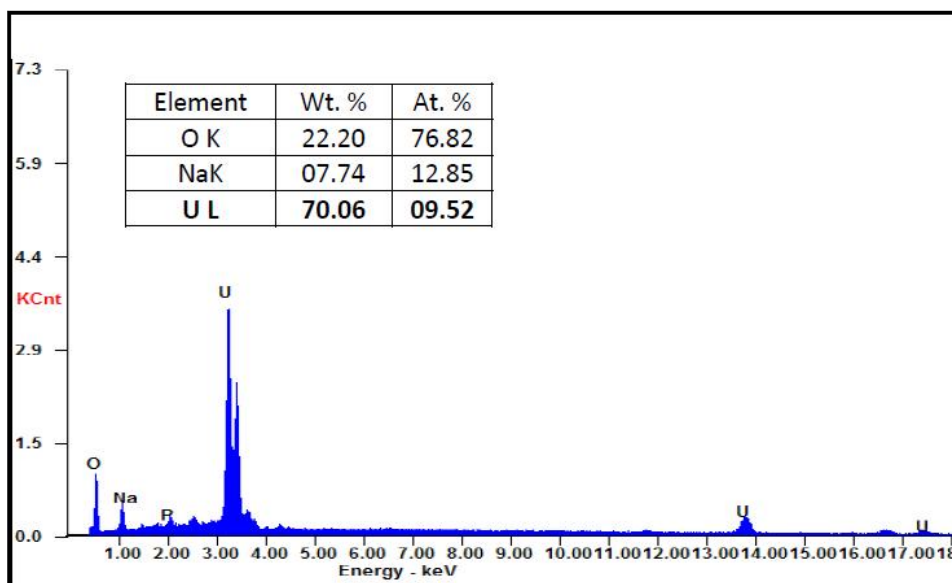


Figure 9 : ESEM of the sodium diuranate product

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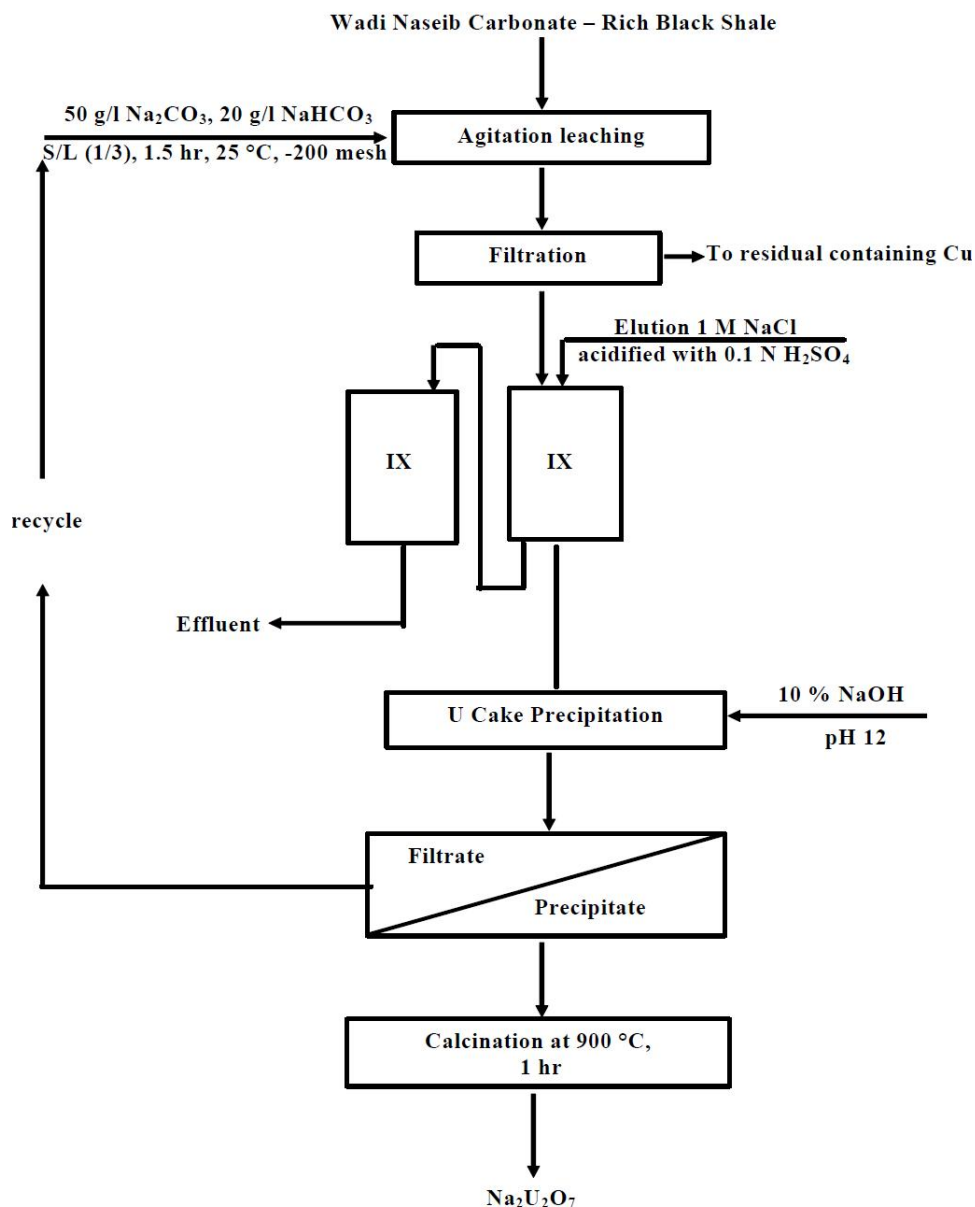
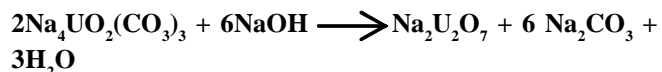


Figure 10 : Proposed technical flow sheet for selective of uranium from carbonate-rich black shale



CONCLUSION

The carbonate rich black shale of W Naseib area at SW Sinai and whose uranium and copper assay attain 1600 and 2.8% respectively, was subjected to selective alkali leaching studies of uranium content. The purpose was to avoid Cu co-leaching of its copper content.

From the studied relevant factors, the optimum values for dissolving about 97% of the uranium con-

tent were summarized as follows:

Alkali concentration	:	50 g/l Na_2CO_3 / 20 g/l NaHCO_3
S/L ratio	:	1/3
Agitation time	:	1.5h
Leaching temperature	:	25°C
Grain size	:	-200 mesh size

Using these factors, 2 L leach liquor assaying 0.39gU/l was prepared for its recovery via the anion exchange Lewatit Monoplus M 500 resin. The obtained eluate have been quantitatively precipitated via sodic decomposition and the obtained diuranate after its calcination was found to assay about

76% uranium.

Finally, all the obtained results have been summarized in the following flow sheet as shown in Figure (10).

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