

An Alternative Procedure for Selective Leaching of Uranium from Carbonate Rich Black Shale, Um-Bogma Formation, El-Allouga, Southwestern Sinai

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Summary: An alternated method is carried out to acquire a selective leaching procedure for uranium from carbonate rich black shale (BS) of southwestern Sinai (0.16% U_3O_8). Uranium was present in the hexavalent state (VI) in the rock sample. This method is based on using a mixed reagent of citric acid/calcium citrate reagent in a manner to leave the carbonate, vanadium and copper almost intact for the later proceeding. The influence of different factors as concentration of citric acid/Ca-citrate, molar ratio, grain size, pH of the leach liquor solutions, S/L ratio, leaching time and temperature was investigated in order to find optimum conditions. The purpose is to formulate economic value that would realize the recovery of leaching a mixed reagent for recycling. From the obtained leach liquor, uranium can be precipitated and recovered by addition of isopropyl alcohol (IPA) to leach liquor.

Introduction

Uranium, as a natural radioactive heavy metal, widely disperses throughout the earth's crust, with an average concentration of less than $4 \text{ mg kg}^{-1(1-3)}$. Much of the known uranium now existing in the world is in ores with uranium contents below 0.2% U_3O_8 . The end product is typically referred to as uranium yellow cake, which is usually sent to a refinery where it is further purified into a form suitable for enrichment and fuel fabrication⁽⁴⁾. Uranium is present in such solutions in the hexavalent state⁽⁵⁾.

Uranium is used worldwide as a fuel for nuclear power reactors to produce electricity^(6,7). The conventional resources of uranium are limited and available in few countries. Uranium recovery from unconventional sources is being explored worldwide for sustainable nuclear power generation⁽⁸⁻¹⁴⁾.

Black shale (BS) is a valuable unconventional source of uranium. The uranium content present in the carbonate rich black shale, the studied ore material sample was collected from El-Allouga area which is located in SW Sinai between long. $33^\circ 25'$ and $33^\circ 26'$ E and lat. $29^\circ 02'$ and $29^\circ 04'$ N containing $1600 \text{ ppm}^{(15)}$. Black shale (BS) is sedimentary deposits of the lower member of the early Carboniferous Um Bogma Formation which contains a considerable amount of carbonate minerals.

They did a survey on carbonaceous shales in Egypt^(16,17). If a uranium ore is leached with alkaline carbonate solutions, only the hexavalent uranium will be extracted since the tetravalent uranium will be insoluble in such solutions⁽¹⁸⁾.

On the other hand, ore materials containing a relatively high content of lime-carbonate minerals proved prohibitively expensive when leached by a mineral acid.

By using citric acid/calcium citrate mixture, decomposition of lime-carbonate would not be allowed⁽¹⁹⁾.

Citric acid ($C_6H_8O_7$) is a non-toxic tri-carboxylic acid and it forms ternary mixed metal complexes with various metal ions involving the carboxyl and hydroxyl groups. It is commonly used as a chelating/complexing agent for the extraction of actinides, radionuclides and heavy metals from contaminated soils and geologic rock minerals^(20,21). It has actually been realized for uranium by using citric acid and calcium citrate mixture in a proper solid / liquid ratio⁽²²⁾. The latter has been based upon the fact previously observed by⁽²³⁾ has found the presence of calcium citrate would hinder tricalcium phosphate solubilization.

This is due to the fact that carbonate rich black shale is not amenable to alkaline leaching and that even when leached by mineral acids, carbonate, vanadium and copper are dissolved with subsequent difficulties in recovering the former⁽²⁴⁾. On the other hand, in case of lime carbonate rich ore type, it would hinder economic treatment with alkaline reagents. In this paper, we are able to overcome these difficulties by selective leaching of uranium content from such an ore material by citric acid in a proper ratio of calcium citrate.

Uranium has previously been selectively leached from Abu-Tartur phosphate deposits using a citric acid/calcium citrate mixture. Thus, while uranium is completely leached, the phosphate mineral is left intact^(25,26).

This paper was focused on an alternated method which is carried out to acquire a selective leaching procedure for uranium from carbonate rich black shale (BS) using a mixed reagent of citric acid/calcium citrate reagent in a manner to leave the carbonate, vanadium and copper almost intact for the later proceeding.

Experimental

Materials and equipments

All chemicals and reagents used in the present work were of analytical grade and purchased from Aldrich. All experiments were carried out using double distilled water and Whatman filter paper No. 40. The stock solution containing uranium was prepared by dissolving its corresponding nitrate salt in water. Holland Inolab pH meter was used for pH measurement. Barnstead water purifying was used for supplying double distilled water. Atomic Absorption Spectrometer GBC 932 AA (UK) was used for the determination of vanadium and copper in the leach liquor solutions. The waste 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.

Experimental procedures

Selective leaching of uranium

Several experiments have been performed to determine the selectively combined leaching conditions of uranium from the studied black shale using mixed reagents. The studied conditions involved the different mixed reagents, concentration of mixed reagents, molar ratio, the effects of grain size, pH, a solid/liquid ratio, reaction time and temperature. In these experiments, 40 g sample portions of the working black shale were used.

Direct precipitation of uranium

The present work deals with uranium recovery from such leach liquors in a way involving non-destruction of the valuable reagents used in leaching. By evaporation the calcium citrate can be precipitated and used for recycling as leach reagents. If alcoholic as isopropyl alcohol (IPA) is added to leach liquor and the relatively dilute pregnant liquor, excessive volumes of the alcohol will be necessary for a complete separation of calcium citrate. It is also interesting to refer that uranyl citrate well before the complete separation of calcium citrate. After addition of isopropyl alcohol (IPA), the filtrate containing isopropyl alcohol (IPA) and citric acid is subjected to about 70°C to recover citric acid for recycle as well as the alcohol after condensed. Therefore, separation of uranyl citrate from calcium citrate, the salted out salts are only composed of uranyl citrate and calcium citrate representing about 36% of the originally added quantity. For the separation of these two salts, use was made of the extremely wide difference in their water solubility (uranyl citrate is greatly soluble while calcium citrate solubility is 0.9 g/L). Water is then added in a solid/liquid ratio 1/1 where uranyl citrate dissolves almost completely calcium citrate not dissolved and recycled used. The pregnant uranyl citrate is then subjected to 10% sodium hydroxide at pH equal 7; uranium was precipitated and dried at 110°C for 1 hour, the sodium diuranate $\text{Na}_2\text{U}_2\text{O}_7$ prepared and analyzed by SEM.

Analytical control procedures

U Control Analysis

For the control analysis of all the performed experiments, uranium was analyzed in all the working stream solutions volumetrically by the oxidimetric titration method using ammonium metavanadate in the presence of diphenylamine sulfonate indicator until its color end point changes to slightly violet color⁽²⁷⁾.

Control analysis of CaO

For the determination of the calcium content in the different stream solution samples, the compleximetric titration method against a standard EDTA solution in

presence of murexide indicator was used⁽²⁸⁾. This indicator has a blue violet color in alkaline solution at pH 12. For this determination, it is necessary to add about 30 mg of potassium cyanide and 30 mg of hydroxylamine hydrochloride to 1 ml of each sample solution and adjusting the pH to 12.

Analysis of the product

Finally, the precipitated sodium diuranate $\text{Na}_2\text{U}_2\text{O}_7$ product was analyzed in the NMA Labs by XL30 Philips type (SEM) scanning electron microscope.

Results and discussion

Optimization of the selective leaching conditions

The working carbonate rich black shale BS has been completely analyzed⁽¹⁵⁾ for its major elements as well as trace elements together with the study interesting metal value of uranium. According to the obtained results as shown in Table (1), it can be stated that:

The XRD analysis of the studied sample has indicated that ankerite ($\text{Ca, Mg, Fe}(\text{CO}_3)$) is the main carbonate mineral constituent while the clay content is represented by the three principal clay minerals, viz, kaolinite, montmorillonite and illite Fig. (1). In the meantime, the other mineral constituents involve quartz, gypsum besides hematite minerals.

Counts

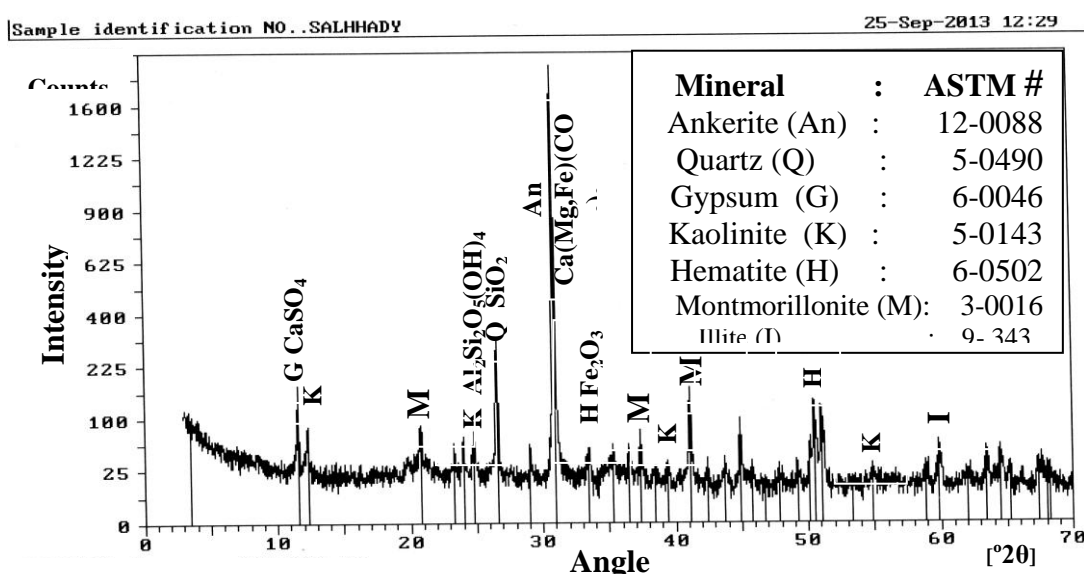


Fig. (1): XRD Pattern of the working carbonate-rich black shale BS sample

As previously mentioned, the working sample of the studied 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 shown in Tables (1), 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 meantime, iron content is equivalent to about 10% Fe₂O₃ besides 1.4% MnO and 0.05% Na₂O and 3.05% SO₃. Among the major oxides, it was revealed that copper assays up to about 2.8%.

Table (1): The chemical analysis of the working sample BS 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	
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		

* **L.O.I:** Total Loss of Ignition at 1000°C, *U as element (chemically analyzed).

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 in the extent of 1530 and 1140 ppm as Co₃O₄ and NiO respectively while uranium assays 1600 ppm.

Effect of acid/its salt mixture type

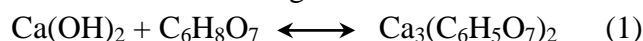
To study the effect of the acid/its salt mixture type and concentration of the study five mixtures, a certain weight portion of the study representative sample of Black Shale BS was agitated in the concerned acid under specific conditions. The latter involved a S/L ratio of 1/2 for a reaction time of half an hour at room temperature and using ore samples ground to -200 mesh (-74 μ) while the applied mixture type concentration involved molarities (1:1), 0.04 mol/L. The obtained results are shown in the Table (2).

The metal recovery was calculated using the data given by the atomic absorption spectrometer, according to the formula: % recovery = $A_e/A_i \times 100$, where A_e = Amount of metal in leached solution and A_i = Initial amount of respective metal in ore.

Table (2): Effect of mixture type upon the selective leaching of uranium from BS

1:1 Mixture type, M	Leaching efficiency, %			
	U	V	Cu	CaO
Formic acid/ Ca-formate	1.60	1.00	1.10	0.10
Acetic acid/ Ca- acetate	2.90	1.70	2.30	0.15
Tartaric acid/ Ca-tartrate	4.20	2.60	3.50	0.20
Citric acid/ Ca-citrate	10.90	Nil	Nil	Nil
Oxalic acid/ Ca-oxalate	7.00	4.10	5.30	1.00

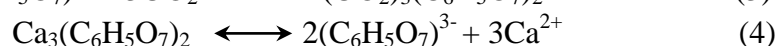
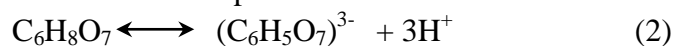
The formation of calcium citrate by the reaction of citric acid with calcium hydroxide represented as in the following reaction:



The reaction mechanism makes use of the ability of citric acid to form stable uranium complexes and calcium citrate incorporated; the ability of citrate anion to form un-ionized associated compounds with calcium ions would be hindered in a manner to prevent decomposition of lime carbonate mineral, vanadium and copper.

Uranium was present in hexavalent state (VI) in the rock sample. Uranium was more completely dissolved in citric acid/calcium citrate mixture reagents. It was indicated that from the results the following: a maximum uranium solubilization (10.90% U_3O_8) was obtained higher concentration of citric acid/calcium citrate as shown in Table (1), uranium was dissolved as uranyl citrate complex $[(\text{UO}_2)_3(\text{C}_6\text{H}_5\text{O}_7)_2]$ with no leaching for CaO and high leaching for uranium from BS. Furthermore, we seek to study citric acid/Ca-citrate factors in the following paper.

Citric acid contains three carboxylic groups ($\text{PK}_{a1}=3.13$, $\text{PK}_{a2}=4.76$ and $\text{PK}_{a3}=6.39$) and one hydroxyl groups ($\text{PK}_{a4}=10.82$) at 25°C as possible donators of protons⁽²⁹⁻³²⁾. When mixture reagents are dissolved (or leached) in aqueous solution and the uranyl ion (UO_2^{2+}) are present in the leach liquor, a complexation/chelating reaction may take place. The overall reaction after leaching of citric acid/calcium citrate for carbonate rich black shale can be represented as follows:



Effect of citric Acid / calcium citrate molarity

To study the effect of the mixed selective leaching reagents of citric acid/calcium citrate concentrations upon the selective leaching efficiency of uranium from BS, seven leaching experiments have been performed at room temperature using different concentrations. While the latter was ranged from 0.01 to 0.12 mol/L for each, -200 mesh (-74 μ), the S/L ratio was fixed at 1/2, the leaching time was fixed at only half an

hour and all experiments at room temperature. From the obtained results shown in Table (3), it was found that by increasing the molarity of the selective leaching reagents, the leaching efficiency of uranium has progressively been increased. Thus, while the uranium leaching efficiency has varied between about 3.1% and 12.3% leaching efficiency at 0.06 mol/L of mixed selective leaching reagents, at the input reagent concentrations of 0.01 and 0.12 mol/L respectively. On the other hand, it is quite interesting to mention that the leached calcium value is quite low and has been increased from 2.2 raised to only 4.5% at the input mixed reagents molarity of 0.08 and 0.12 mol/L respectively.

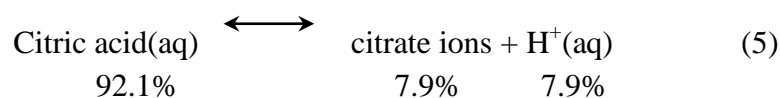
Table (3): Effect of citric acid/Ca-citrate concentration upon the selective leaching of uranium from BS

1:1 Citric acid/Ca-citrate, M	Leaching efficiency, %			
	U	V	Cu	CaO
0.01	3.10	Nil	Nil	Nil
0.02	5.50	Nil	Nil	Nil
0.04	10.90	Nil	Nil	Nil
0.06	12.30	Nil	Nil	Nil
0.08	17.10	0.07	0.20	2.20
0.1	19.80	0.10	0.32	3.40
0.12	24.00	0.12	0.41	4.50

From the above obtained results, accordingly, in the following experiments, 0.06 mol/L citric acid/Ca-citrate mixed reagent will be used to study the selective leaching of uranium from BS at different leaching conditions.

Laboratory bench-scale, many experiments were conducted to determine the efficiency of citric acid/calcium citrate reagent mixture to extraction of uranium from carbonate rich black shale. The results indicate that citric acid is highly effective in leaching uranium, extraction efficiency increase with increasing citric acid concentration and the enhanced leaching of U(VI) in the presence of calcium citrate, including the complexation of U(VI) with citrate⁽³³⁾.

The dissociation of calcium citrate to citrate ions to form another complex with uranium and calcium ions which replacements and calcium were leached from carbonate lime which represented in the following reactions as follow:



Effect of molar ratio

In a trial to improve the leaching conditions, another experimental leaching series was performed using a different molar ratio from citric acid/Ca-citrate as (1:1, 2:1, 3:1, 4:1 and 5:1). In these experiments, the leaching conditions were kept fixed as citric acid/Ca-citrate 0.06 mol/L, -200 (-74 μ), in a solid/liquid ratio of 1/2, only half an hour leaching time at room temperature.

Table (4): Effect of molar ratio upon the selective leaching of uranium from BS

Molar ratio of Citric acid/Ca-citrate	Leaching efficiency, %			
	U	V	Cu	CaO
1:1	12.30	Nil	Nil	Nil
2:1	16.71	0.14	0.43	4.80
3:1	18.45	0.19	0.63	6.70
4:1	20.36	0.26	0.88	7.53
5:1	23.73	0.43	1.03	9.60

From the results shown in Table (4), it is evident that (1:1) molar ratio which selective leaching of uranium only without leaching of V, Cu and CaO. Therefore, (1:1) molar ratio of 0.06 mol/L citric acid/Ca-citrate could be considered as optimum molar ratio.

Effect of grain size

Regarding the effect of the particle size of samples BS upon the selective leaching of uranium from BS, different samples of the latter were ground to different particle size ranging from completely passing through mesh sizes -50 (-297 μ), -70 (-210 μ), -100 (-149 μ), -150 (-100 μ), -200 mesh (-74 μ) and -230 (-63 μ). The obtained samples were then leached using 0.06 mol/L citric acid/Ca-citrate of S/L ratio of 1/2 for 30 min. at room temperature. From the obtained results shown in Table (5), it is clearly evident that by decreasing the particle sizes from -50 to -200 mesh sizes, the selective leaching efficiency of uranium has increased from 6.0 to 12.3% respectively, while the equivalent calcium minerals has no leached and by increasing mesh size to -230, the beginning the dissolution of vanadium, copper and carbonate.

Table (5): Effect of particle size upon the selective leaching of uranium from BS

Particle size, mesh	Leaching efficiency, %			
	U	V	Cu	CaO

-50	6.00	2.30	2.90	4.10
-70	7.70	1.70	1.91	2.10
-100	9.80	0.80	0.23	1.23
-150	11.20	0.16	0.18	0.94
-200	12.30	Nil	Nil	Nil
-230	13.52	0.12	0.19	1.10

From the obtained data, it can be concluded that the -200 mesh (-74 μ) is the best mesh suitable to selective leaching of uranium and leave vanadium, copper and calcium without leaching. Further, we can use this mesh in following all experiments.

Effect of pH

The selective leaching of U(VI) with citric acid/Ca-citrate was studied at various pH values. The other variables were fixed at 0.06 mol/L citric acid/Ca-citrate, 1:1 molar ratio, -200 mesh (-74 μ), S/L ratio (1/2), 30 min. at room temperature. The data presented in Table (6) show that the leaching efficiency of uranium increases with increasing of pH in acidic medium until it reaches pH (5.7) neutral medium which gives the higher leaching of U(VI) without leaching of V, Cu and CaO and by increasing pH alkaline medium the leaching efficiency of uranium decreasing and increasing the leaching efficiency of V, Cu and CaO.

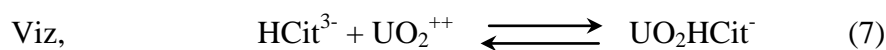
Table (6): Effect of pH upon the selective leaching efficiency of uranium from BS

pH	Leaching efficiency, %			
	U	V	Cu	CaO
0.5	15.70	1.40	4.8	5.4
0.8	14.60	1.20	4.3	4.8
1	14.20	1.00	4.1	3.7
1.3	13.40	0.80	3.4	3.1
1.8	12.30	0.50	3.2	2.7
2.2	12.90	0.30	2.7	2.3
2.5	12.30	0.20	2.5	2
2.9	11.90	0.10	2.3	1.7
3.1	14.60	0.09	1.9	1.3
3.6	15.50	0.08	1.7	1.00
4	16.40	0.05	1.2	0.60
4.5	16.80	0.03	0.5	0.50
5	17.60	Nil	0.2	0.10
5.7	18.90	Nil	Nil	Nil
6	15.00	0.70	1.80	0.20
7	13.10	1.90	3.90	0.20
8.3	11.30	2.20	5.90	0.20

The high values of leaching efficiency of uranium in neutral medium explained by the dissolution of Ca-citrate to Ca^{2+} and citrate ions and by dissolution of carbonate, the Ca^{2+} ions from Ca-citrate can be a replacement in carbonate in neutral medium which further decreases the dissolution of V, Cu and CaO.

The ability to form stable uranium complexes in acid, neutral and basic solutions of pH's is less than 9. The stoichiometric ratio of uranium to citrate in the complex is unity in acid solutions⁽³⁴⁾ while in neutral and basic solutions the ratio is probably 2:3⁽³⁵⁾. At pH's above 9, the complex decomposes forming uranyl hydroxide. Insolubilization of the lime-carbonate mineral was made possible by adding calcium citrate to citric acid.

Regarding uranium chemistry in citric-citrate acid solutions⁽³⁶⁾, have spectrophotometrically found that the stoichiometric ratio of uranium to citrate in the complex is unity in the pH range of 3 to 4.5⁽³⁷⁾, have also potentiometrically indicated that in citrate solutions of pH's ranging from 2 to 4. A monovalent uranyl citrate anion complex is formed through the dissociation of the three hydrogens from the carboxyl groups of citric acid;



On the other hand^(34,38) in their study of possible uranyl complex formation in citric acid media of relatively low pH values used a uranyl ion concentration in the range of $10^{-5} - 10^{-6}$ (to eliminate polymerization). These authors have found that three kinds of complexes 1/1 uranium to citrate ratio could actually be found in the pH range of 2.2 to 2.9; namely, $[\text{UO}_2\text{H}_3\text{Cit}]^+$, $[\text{UO}_2\text{H}_2\text{Cit}]$ and $[\text{UO}_2\text{HCit}]^-$. The $[\text{UO}_2\text{H}_3\text{Cit}]^+$ complex is the predominant species at pH's lower than 2, while a mixture of the three complexes is in the pH range 2-3, whereas at pH's above 3, the complex is mostly in the form $[\text{UO}_2\text{HCit}]^-$.

From the obtained results as shown above in Table (6), the dissolution efficiency of uranium increases gradually by increasing pH from 0.5 to 5.7 where they attained 15.7% to 18.9% uranium leaching efficiency respectively. This extends pH up to 5.7 where the dissolution efficiencies decreased to 11.3% at pH 8.3; this decrease may be due to formation of some complexes which have led to uranium reprecipitation. Therefore, it can be concluded that a pH 5.7 would be considered as an optimum pH for selective leaching of uranium from BS.

Effect of the solid/liquid ratio

To study the effect of the solid/liquid ratio upon the selective leaching efficiency of uranium from BS working sample, a series of experiments has been performed using an acetic acid concentration of 0.06 mol/L, upon -200 mesh (-74 μ) ore samples for only half an hour leaching time at room temperature while the S/L ratio was varied between 1/2 up to 1/9.

Table (7): Effect of S/L ratio upon the selective leaching of uranium from BS

S/L ratio	Leaching efficiency, %			
	U	V	Cu	CaO
1/2	18.90	Nil	Nil	Nil
1/3	20.20	Nil	Nil	Nil
1/4	28.40	Nil	Nil	Nil
1/5	35.40	Nil	Nil	Nil
1/6	47.10	Nil	Nil	Nil
1/7	53.00	Nil	Nil	Nil
1/8	67.10	Nil	Nil	Nil
1/9	69.00	1.50	1.98	5.40

From the obtained results shown in Table (7), it can be deduced that at the S/L ratios of 1/2 to 1/8, the selective leaching of uranium increases from 12.3 to 67.1% respectively without the leaching of CaO. Increasing the S/L ratio to 1/9, the CaO has started to be leached 5.4%. Therefore, the S/L of 1/8 would be considered as an optimum value.

Effect of leaching time

Using a citric acid/Ca-citrate concentration 0.06 mol/L and ore samples ground to -200 mesh (-74 μ) in a S/L ratio of 1/8 at room temperature, the effect of the leaching time was studied in the range from 30 up to 90 min. and the obtained results are tabulated in Table (8). From the latter, it was clearly evident that almost all the CaO has been no leached (Nil) but at the leaching time of 90 min. and at which the CaO has been leached and reached 6.5% leaching efficiency. Thereafter, the latter has started to be leached and therefore the reaction time of 75 min. would be considered as an optimum value at which the CaO will remain intact.

Table (8): Effect of the reaction time upon the selective leaching of uranium from BS

Time, min.	Leaching efficiency, %			
	U	V	Cu	CaO
30	67.10	Nil	Nil	Nil
45	70.00	Nil	Nil	Nil
60	73.4	Nil	Nil	Nil
75	77.50	Nil	Nil	Nil
90	78.20	1.45	2.31	6.50

Effect of temperature

In order to reduce the heat energy and in turn of the leaching costs, different temperatures were studied in the range of 25 to 65°C under the other leaching factors which were fixed at citric acid/Ca-citrate concentration 0.06 mol/L and ore samples ground to -200 mesh (-74 μ) in a S/L ratio of 1/8 for 1.25 h. The resultant leaching efficiency as shown in Table (9) reveals that increasing the leach temperature has brought an increasing effect where in the studied range; the uranium leaching efficiency has increased from 77.5% at 25°C and to 96% thereafter. This is most probably due to the increased reaction temperature which would increase the leaching efficiency of CaO above 45°C which reaches 12.5% at 65°C. Furthermore, the 45°C is considered as the optimum leaching temperature.

Table (9): Effect of the temperature upon the selective leaching of uranium from BS

Temperature, °C	Leaching efficiency, %			
	U	V	Cu	CaO
25	77.50	Nil	Nil	Nil
35	90.90	Nil	Nil	Nil
45	94.00	Nil	Nil	Nil
55	96.00	3.65	6.98	7.00
65	98.00	6.96	8.90	12.50

It is a great advantage of organic acid(s) that increase the solubility of metal ions at (neutral) pH by complexation and thereby, precluding the precipitation of metal(s) as their hydroxides successfully. The anions and the protons of organic acids are able to leach metals by acidolysis and/or complexation phenomenon.

Finally in this work, we observed that calcium citrate hinder the solubilization of carbonate mineral, vanadium and copper; a matter which is due to the ability of the citrate anion to form un-ionized associated compounds with calcium ions. Thus, while uranium can form stable uranium complexes with citric acid on one hand, presence of calcium citrate would hinder carbonate, vanadium and copper solubilization.

Recovery of uranium

A 100 g sample portion of the working BS sample was subjected to the above studied optimum conditions of its citric acid/Ca-citrate leaching, after filtration and proper washing of the obtained waste by distilled water until the volume of liquor to attain up to volume 1 L. The obtained leach liquor was found to be uranium assay attained 0.15 g/L U, while the assay of V₂O₅, CuO and CaO attained 0.05 g/L, 0.10 g/L and 0.73 g/L, respectively. Furthermore, we make analyses for the waste by XRF in NRC labs as shown in Table (10).

Table (10): The chemical analysis of the waste after selective leaching using citric acid/Ca-citrate by XRF in NRC

Component	Wt. %	Component	Wt. %
SiO ₂	15.60	K ₂ O	0.90
Al ₂ O ₃	8.00	TiO ₂	0.80
Fe ₂ O ₃	10.00	P ₂ O ₅	0.07
MgO	5.40	SO ₃	3.00
MnO	1.40	Cl	0.04
CaO	18.90	CuO	2.77
Na ₂ O	0.05	L.O.I*	30.00
Total		96.94	
Trace elements	Wt. %	Trace elements	Wt. %
Cr ₂ O ₃	0.030	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	0.028	*U	0.004
ZrO ₂	0.070		

* **L.O.I:** Total Loss of Ignition at 1000°C, *U as element (chemically analyzed).

Precipitation of uranium

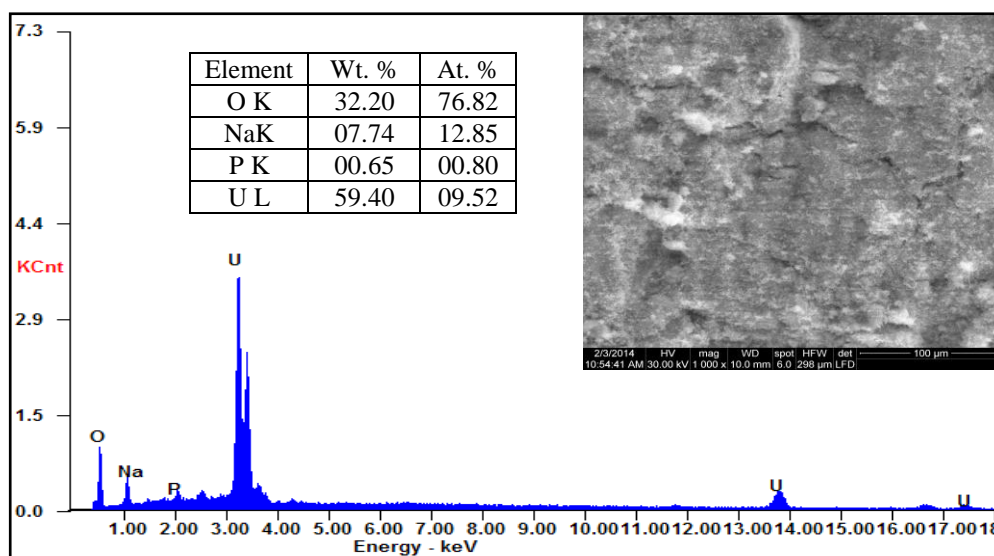
Recovery of uranium from the obtained pregnant citrate leach liquors was carried out via methylation (salting-out) by isopropyl alcohol (IPA) for citric acid-citrate separation after concentrating the obtained large volume of leach liquors by evaporation.

If isopropyl alcohol (IPA) added to leach liquor, and due to relatively dilute pregnant liquor, different volumes of the isopropyl alcohol (IPA) will be added for a complete separation of calcium citrate as shown in Table (11).

Table (11): Separation of citric acid-calcium citrate by isopropyl alcohol (IPA)

Original l.		Concentrated l. (2X)		Highly concentrated l. (6X)		Very Highly concentrated l. (8X)	
Ag./Alc. Ratio	Salted out Ca- Cit., %	Ag./Alc. ratio	Salted out Ca- Cit., %	Ag./Alc. Ratio	Salted out Ca- Cit., %	Ag./Alc. ratio	Salted out Ca- Cit., %
1/1	12.00	1/1	29.00	1/1	55.00	1/1	79.6
1/2	29.00	1/2	45.70	1/2	72.3	1/2	93.2
1/3	33.30	1/3	79.00	1/3	91.8	1/3	98.5
1/4	50.10	1/4	93.40	1/4	98.4	-	-
1/5	67.10	1/5	98.00	-	-	-	-
1/6	92.10	-	-	-	-	-	-
1/7	97.90	-	-	-	-	-	-

The pregnant uranyl citrate is then subjected to 10% sodium hydroxide at pH equal 7; uranium was precipitated and dried at 110°C for 1 hour, the sodium diuranate $\text{Na}_2\text{U}_2\text{O}_7$ prepared and analyzed by SEM.

**Fig. (2): SEM image and EDX analysis of the uranium product**

Conclusions

Uranium could be selectively leached from carbonate rich black shale by a proper mixture of citric acid/calcium citrate. Uranium was recovered from the obtained leach liquor via methylation after its evaporation, extraction and precipitation, followed by drying to produce sodium diuranate. The flow sheet is given in Fig. (3). However, in order to minimize the cost of uranium recovery, this can be done through recycling all reagents and chemicals in all experiments.

The studied relevant conditions that have realized this objective were found to involve:

Citric acid/Ca-citrate concentration: 0.06 mol/L

Citric acid/Ca-citrate molar ratio: 1:1

Grain size: -200 mesh (-74μ)

pH: 5.7

S/L ratio: 1/8

Leaching time: 1.25 h

Temperature: 45°C

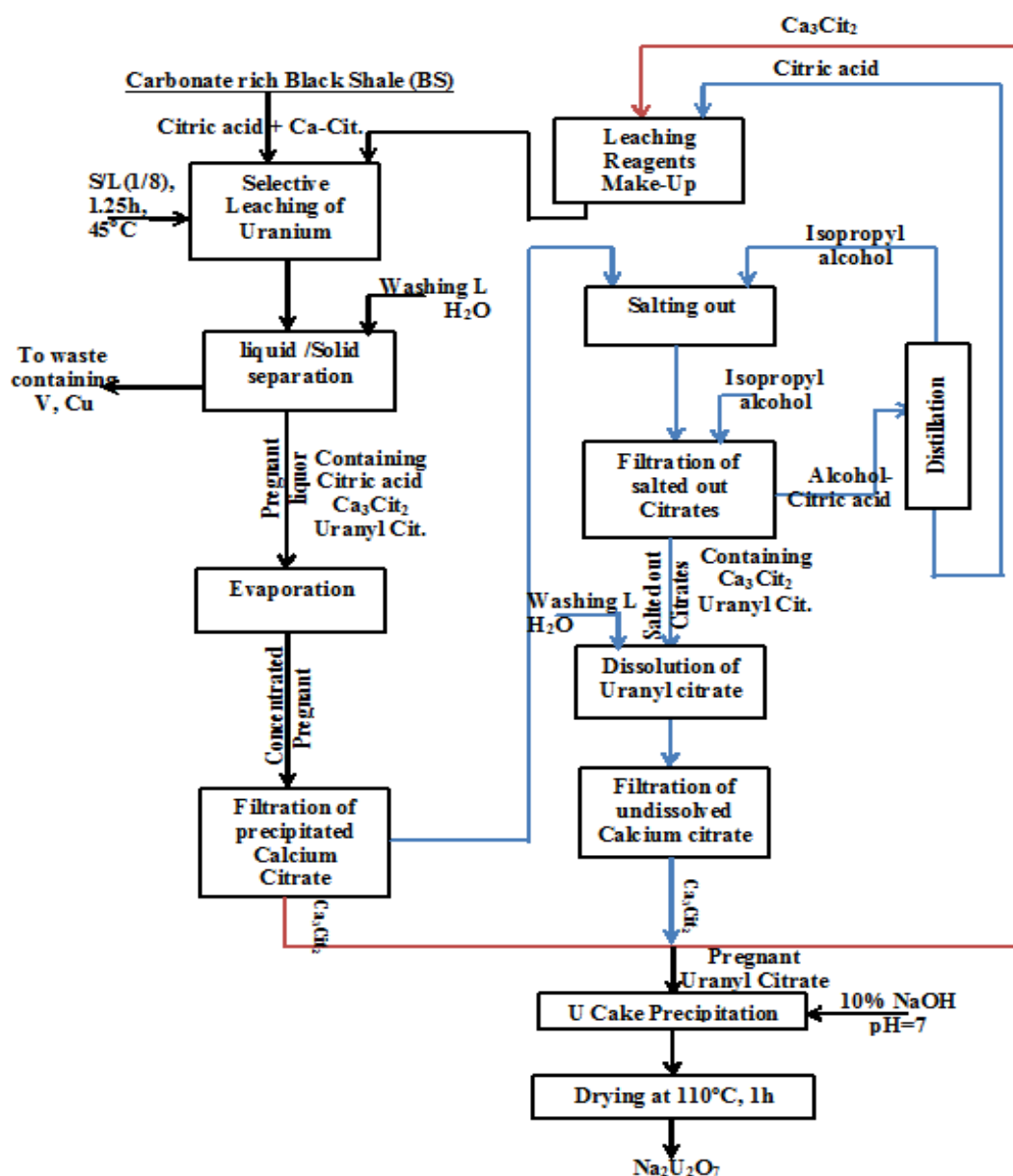


Fig. (3): Flow sheet for the recovery of sodium diuranate from El-Allouga carbonate rich black shale BS

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