



Percolation Leaching and Uranium Recovery of El Erediya Granitic Rocks, Eastern Desert, Egypt.

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خلاصة

تتواجد رواسب اليورانيوم في منطقة العرضية على مشارف المسافة من طريق فناسفاجا بوسط الصحراء الشرقية المصرية، ولقد أعدت عينة تكنولوجية تزن 50 كجم لهذه الدراسة. أثبتت الدراسة المعدنية أن معدن اليورانوفين هو معدن اليورانوم الرئيسي الذي يتواجد على هيئة صفائح صفراء وأيضاً حبيبات ابرية تملأ الكسور والشقوق بينما تتكون معادن الشوائب في الغالب من معادن الكوارتز والفلسبار المتحول ونسبة قليلة من البلاجو كليز، أما التحليل الكيميائي لهذه العينة فإنه كالتالي : (36 و 74٪ س أ، 81 و 13٪ لو 2 أ، 091٪ يورانيوم)

وقد استخدم أسلوب الإذابة التخليلية بمحلول حمض الكبريتيك المخفف عند درجة أس هيدروجيني منخفض، كما درست العوامل المؤثرة الأخرى على عملية الإذابة مثل الحجم الحبيبي ووقت الإذابة وقد أوضحت الدراسة أن أكثر من 97٪ محتوى اليورانوم قد أمكن إذابته بعد ستة أسابيع عند درجة أس هيدروجيني 4 و 1 بينما بلغ تركيز اليورانوم في المحلول الحامل على 2 و 1 جم يورانيوم/لتر وذلك باستخدام نظام متعدد المراحل إذابة.

أثبتت الدراسة أيضاً أن ثلاث أوكتيل أكسيد الفوسفين (TOPO) بتركيز أو جزئي والمخفف بالكيروسين هو أحسن المذيبات المضوية لاستخلاص الوارانيوم من محلول الإذابة وذلك في وجود تركيز من حامض أو جزئي النيتريكي.

هذا وقد استخدم لاسترجاع اليورانوم بكفاءة محلول كربونات الصوديوم بلغت نسبة الإسترجاع 99٪ من أصل اليورانوم في محلول الإذابة. كما أمكن ترسيب أكثر من 98٪ من محتوى اليورانوم على صورة ثنائي يورانات الصوديوم باستخدام طريقة التحليل الصوديومي

كما أمكن تصميم بوحدة تشغيل مقترحة على أساس استخلاص اليورانوم من جرانيت العرضية بعائد عام يصل إلى حوالي 90٪ من محتوى اليورانوم الأصلي.

Abstract

El Erediya uranium occurrence is located in the vicinity of Qena-Safaga road, Central Eastern Desert. A bulk head sample of about 50 Kg was prepared for this study.

Mineralogically, uranophane is the essential uranium mineral identified in the studied bulk head sample. It occurs as yellow flakes and acicular grains filling fractures, whereas the gangue minerals are mainly composed of quartz, altered potash feldspar, and minor plagioclase. The head sample assays as 74.36% SiO₂, 13.81% Al₂O₃ and 0.091% U.

Percolation leaching utilizing H₂SO₄ was performed at a fairly low pH value. The examined factors include pH of the leach solution, the grain size beside the duration time. More than 97% leaching of the uranium was reported after percolating the leach solution for 6 weeks at pH 1.4. Thus it could be possible to produce a pregnant leach solution assaying more than 1.2 gU/L by using a multi-stage leaching system.

For recovering uranium, tri-octyl-phosphine oxide (TOPO) in kerosene was found to be the most powerful U-extractant. Good U-distribution coefficient (E) of 103 has been obtained with 0.1 M TOPO in the presence of 0.1 M HNO₃.

In the stripping circuit 0.2 M Na₂CO₃ solution was found efficient and more than 99% of U was reported to the aqueous phase as uranyl tricarbonate (UO₂(CO₃)₃)⁴⁻.

By applying sodic decomposition up on the stripping carbonate solution, more than 98% of U was precipitated as sodium diuranate (Na₂U₂O₇).

A proposed flowsheet was designed to recover U from El Erediya granites with an overall recovery of about 90%.

Introduction

The work presented here is mainly concerned with mineralogical and percolation leaching studies of the uraniumiferous granitic rocks of El-Erediya area. The latter is located at the Central Eastern Desert, south-east of Gebel Erediya and is bounded by latitudes 26° 17' and 26° 27' N and by longitudes 33° 27' and 33° 29' E.

The uranium mineralization in the investigated area is found to be related to N-E trending shear zone in pink coarse grained granite. A massive red jasperoid vein of 50-150 cm thick occupies the median part of the shear-

zone. The disseminated secondary uranium minerals are sparsely found on the surface within the shear-zone and its country rock [1].

Mineralogical identification using X-ray powder data (XRD) applied on the mineralized surface samples revealed the presence of secondary uranium minerals; namely uranophane, β -uranophane, soddyite and renardite. The most abundant mineral is uranophane [2].

The distribution and the relatively small estimated reserves of the secondary uranium mineralizations in El-Erediya granitic rocks would not justify the construction of a conventional leaching plants. For this reason, leaching studies must be directed for developing non-conventional processes at the mine, so that the leaching-recovery system could be easily portable.

Natural leaching has actually been applied for uranium recovery from low-grade ores [3-6]. According to Freire de Andrade et al [7], natural leaching has the advantage of requiring a reduced amount of equipment, since the bulky operations such as milling, conventional leaching and thickening are eliminated.

On the basis of the above givings, the process for recovering uranium from the granitic rocks of El Erediya has been formulated and developed in this study as follows:

- a) Multi-stage percolation leaching of uranium is done under controlled acidity.
- b) Recovery of uranium form the leach solution is accomplished by means of the solvent extraction technique.
- c) Precipitation of uranium from the pregnant stripping solution is achieved by sodic decomposition.

Mineralogical Investigation and Chimiical Assay of the Head Sample

The main gangue minerals in the comminuted head sample consist of quartz plus highly altered potash feldspars (including both microcline and orthoclase) and possibly minor plagioclase.

Gravity fractionation using methylene iodide of specific gravity 3.14 revealed the presence of 2.34% by weight as sink fraction and was found to assay 5.16% eU. The latter was mainly contained secondary U-minerals identified as uranophane ($\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$). This uranium mineral was found to occur in bundles of acicular needles and occupy fracture planes and vesicles made up of opaline silica between the crushed angular

grains of the rock forming minerals.

Chemical and semi-quantitative XRF analyses were performed on the composite head sample. Data of these analyses are presented in Table (1) and indicate that the head sample is mainly composed of quartz and feldspars as the silicic gangue minerals which are equivalent to about 88.5% oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3$). These inert oxides are in favour of using an acidic leaching solution.

Table (1) Chemical assay of El Erediya granitic rock head sample

Ingredient	Wt. %	Ingredient	Wt. %
SiO_2	74.63	Na_2O	3.52
Al_2O_3	13.81	K_2O	4.62
Fe_2O_3	1.77	MgO	0.07
P_2O_5	0.02	CaO	0.27
TiO_2	0.70	U	0.09
MnO_2	0.15	L.O.I	0.24
Sub-total	91.08	Sub-total	8.81

X-Ray Fluorescence (XRF)

0.01 % (Ti, Mn and Ni)

0.01 % up to 0.1 g (Zn, As, Pb, Y and Nb)

Agitation Leaching Tests

Any leaching process depends largely on a number of factors which have to be carefully studied in order to obtain the optimum U-leaching conditions. The studied factors include the grain size, the concentration of acidic solution (H_2SO_4) and the time of leaching. The rate and efficiency of U-leaching depends on the choice of these closely inter-related factors.

A number of agitation leaching experiments were first performed in order to determine the behavior of the study ore material. This was made using 100g of the comminuted head sample together with 100 ml of deionized water in 500 ml beaker. A leaching solution of 250 ml containing a certain amount of (H_2SO_4) was added. After a certain agitation period of leaching, the slurry was filtered and washed as fast as possible. Both the filtered pregnant liquor and the dried residue were fluourometrically analysed for U.

Effect of Grain Size: As in all leaching methods, the specific surface available must control the rate of U-leaching into solution. So the finer the grind, the faster and more complete will be the leach. From the reported data in Table (2), it appears that the U-leache% slightly increases from 97.15 to 97.65% at 10% H_2SO_4 concentration, as the grain size decreases from -36 mesh to -100 mesh screen, afterwhich any decrease in the grain

size has no effect upon U-leaching %. Thus, for leaching El Erediya granitic rock, fine grinding is not necessary. This would be advantageous for the proposed natural leaching.

Effect of H₂SO₄ Concentration: A series of agitation leaching tests were made to determine the effect of H₂SO₄ concentration ranging from 5% to 10% in the leach solution on the U-leaching %. The data represented in Table (2) show that U-leaching % increases from 97.00% to 97.15% as the concentration of the H₂SO₄ increases from 5% to 10%. Thus the improvement is not perceptible and does not warrant any addition of H₂SO₄ above 5%.

Effect of Leaching Time: Tests investigating the effect of the leaching time at 5% H₂SO₄ concentration are shown in Table (2) and indicate that the leaching rate is relatively rapid and a U-leaching % of about 97.05% is attained in 5 hours at room temperature.

As a matter of fact, the obtained data indicate an interaction or rather an interdependence of the leaching time and acid concentration. From the above results, it was found that the optimum conditions for achieving 97% U-leaching % are as follows: -36 mesh as grain size, 5% as H₂SO₄ concentration and 5 hours as the leaching duration time.

Table (2) : Effects of different relevant factors on leachability of U-from El Erediya granitic rock head sample

Grain Size (mesh)	H ₂ SO ₄ concentration %	Leaching Time, (h)	U Leached %
- 36	10	3	97.15
- 85	10	3	97.39
-100	10	3	97.65
- 36	8	3	97.09
- 36	6	3	97.07
- 36	5	3	97.00
- 36	5	1	96.16
- 36	5	2	96.86
-36	5	5	97.06

Percolation Leaching Tests

In the light of the agitation leaching results, it was found greatly advantageous to apply percolation leaching.

A sample of about 500 g of -36 mesh size of ore was thus placed in an especially constructed 10cm diameter glass column of 100 cm length

having a sump at its base for collecting the effluent. The ore sample was supported on a centered glass disc. Before the percolation leaching was allowed to flow the ore sample was conditioned with 100 ml of deionized water, which was just sufficient to wet the ore sample. In the used technique, the ore sample layer was stationary and the leach solution of certain pH value (1.4, 1.6, 2.0 and 2.4) was allowed to percolate or sweep through the ore bed from the bottom to the top of the column at a rate of 25 ml/min. When the leach solution comes into contact with the ore sample, it leaches out the contained U values. The effluent was collected at the end of each 24 hours and an aliquot sample of 5ml was taken for U analysis, after which the collected leach solution adjusted for pH, was then recycled.

By studying the pH curves represented in Fig. (1), it is evident that after the end of the first week, the U-leaching rate and H_2SO_4 consumption were rather high. The U-leached % were 65%, 38%, 8% and 5% for pH values 1.4, 1.6, 2.0 and 2.4 respectively. After that the U-leaching rate decreases and the pH of the leach liquor becomes constant. These results indicate that the process has given a reasonable U-leaching of 97% at pH 1.4 within 6 weeks, with a fairly low acid consumption of about 20 kg/ton. In order to further decrease the H_2SO_4 consumption, and to increase the U-concentration in the pregnant leach solution, it was found necessary to undertake a multi-stage percolation leaching process. This is because practical recovery of uranium form leach solutions by solvent extraction requires rather high levels of U-concentration besides handling reasonable volumes of solutions.

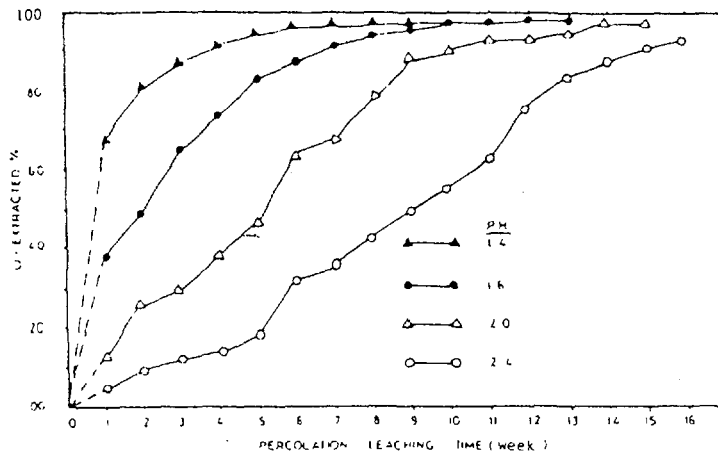


Figure (1) : Effect of PH. and Percolation Leaching Time on U-Extracted % of El Aradiya Granitic Rock

As shown in Fig. (2), the multi-stage process consists of four percolation leaching columns numbered 2, 3, 4 and 5. In each stage leaching was carried out under the same conditions of acidity and flow rate, as in case of a single leaching stage. Make up of the required acidity has been made in order to maintain a pH values of 1.4. The final leach solution after decantation and filtration was found to assay 1.2 g/L U and was considered adequate to be directly pumped to the solvent extraction unit.

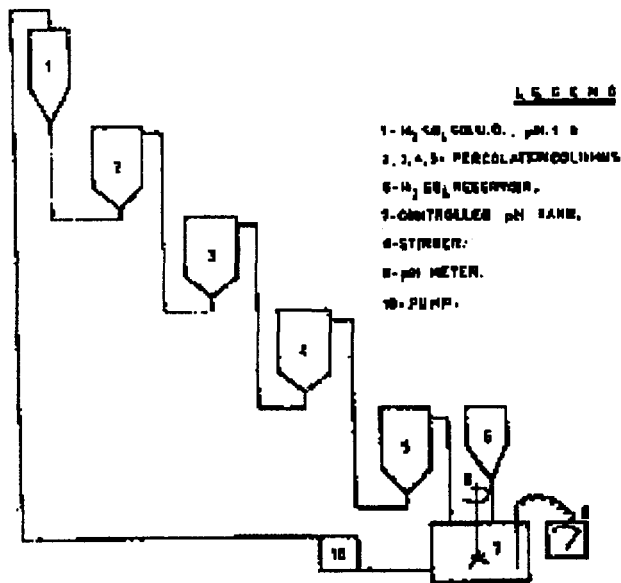


Figure (2) : Proposed Diagrammatic Flowsheet for Multi-Stages Percolating Leaching of Elaradiya Granitic Rock

Uranium Recovery

Solvent Extraction of Uranium

All the solvent extraction experiments were conducted in 150ml ordinary glass separatory funnels. An organic/aqueous (O/A) phase ratio of 1:3 and a contact time of 5 min. were all the time used. Mixing of phases was performed by wrist action shaking. After intimate mixing, the phases were left for settling and the separated the phases were then subjected to U analysis.

Effect of U Concentration: An extraction isotherm has been made using the percolating leach solution at pH 1.4 and 0.1 M TOPO in Kerosene, at an O/A phase ratio of unity for 5 minutes mixing time. It can be seen from Fig. (3), that at 1.2 g U/L as concentration in the aqueous phase, the organic

phase served to load 5.1 g U/L with U extraction coefficient (E) reached 4.2. By increasing the U concentration in the aqueous phase up to 20 g U/L the U(E) decreases to its minimum value of 0.6.

Effect of TOPO and HNO₃ Concentrations: Blake et al. [8] have found that U extraction can be enhanced by adding small amounts of favorable anions like NO₃ or Cl which are particularly effective with phosphine oxide.

Accordingly, a series of tests using the percolation leach solution has been performed using TOPO in Kerosene in two concentrations namely 0.03 M and 0.1 M in the presence of different concentrations of HNO₃ acid ranging from 0.005 M to 0.1 M. Extraction conditions were fixed at an O/A phase ratio of unity and 5 minutes as mixing time. As shown in Fig. (4), the U (E) increases to 80 and 850 at TOPO concentrations 0.03 M and 0.1 M, respectively (i.e. at any concentration of HNO₃, the U (E) increases by approximately 10 folds when TOPO concentration increased from 0.03 M to 0.1 M).

Uranium Stripping: A trial was first made to determine the uranium stripping coefficient (S) from the loaded organic solvent (TOPO) using distilled water, acidic and alkaline solutions. In these tests, the O/A phase ratio and the mixing time were fixed at unity and 5 minutes respectively.

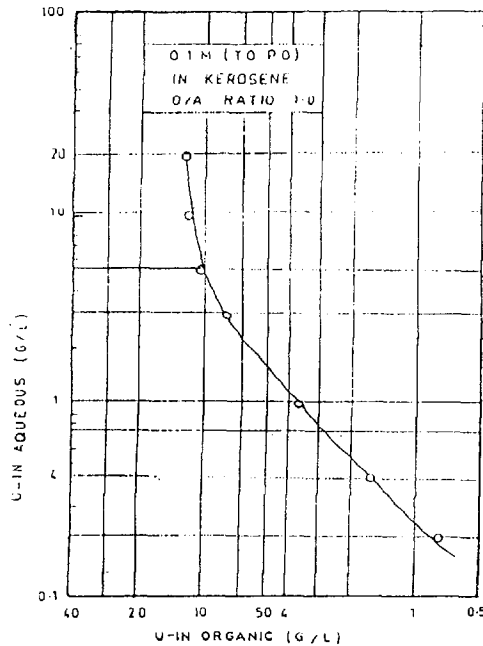


Figure (3) : Uranium Extraction Isotherm From Percolating Leach Sulphate Solution AT pH 1.4

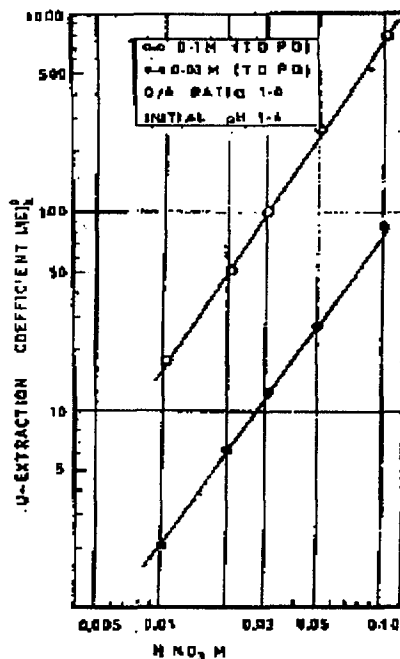
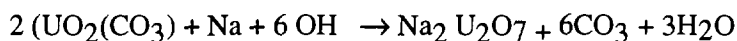


Figure (4) : Effect of HNO₃ Concentration on U(E)_a⁰ At Different (To/Po) Concentration

The obtained U (S) were 0.03, 0.01, 0.04, 0.12, 8.15 and 17 for water, 0.1 M HCl, 0.1 M C₂H₂O₄, 4 M CH₃COOH, 4 M H₃PO₄ and 4 M HF respectively. However, with 0.2 M alkali solutions of NH₄OH, NaOH, (NH₄)₂CO₃, Na₂CO₃, the U(S) were 8.97, 19.24, 30.80 and 667 respectively. It is clearly seen that complete stripping of U was obtained in a single step with 0.2 M Na₂CO₃ solution in where U reports as uranyl tri-carbonate complex ion [UO₂(CO₃)₃]⁴⁻.

Uranium Precipitation: By using sodium hydroxide (NaOH) U could be precipitated from the loaded carbonate stripping solution at pH 11.0 utilizing the well established procedure of sodic decomposition. Thus U was precipitated as sodium-diuranate Na₂U₂O₇ of about 70% U according to the following equation :



Proposed Flowsheet

The foregoing studies were so integrated to construct a proposed flowsheet, Fig. (5) for recovering U from El Erediya granitic rock assaying 0.091% U. The flowsheet consists of the following stages:

Comminution Stage: In this stage, the crude uranium rock sample was

subjected to crushing and grinding using Jaw crusher and roll mill respectively. These mills were adjusted in such a manner that the obtained cominuted material would pass 36 mesh screen.

Percolation Leaching Stage: Multi-stage percolation leach process was successfully applied using acidic solution (H_2SO_4) at pH 1.4 for 6 weeks duration time. Under these controlled conditions, about 97% of U leaching was reported in the obtained pregnant leach solution with a concentration of 1.2 gU/L. This concentration would render the application of the solvent extraction technique more economical.

Uranium Extraction Circuit (SXC): The percolation leach solution (assaying 1.2 gU/L) is directly pumped to the SXC using 0.1 M TOPO in kerosene as the organic solvent. Three counter current extraction stages have resulted in a concentration of 3.3g U/L in the organic phase when using 0.1M HNO_3 as free acidity, 3 min. as a contact time and 1:3 organic/aqueous phase ratio. In order to remove the entrained leach solution from the loaded organic solvent one stage water scrubbing is performed.

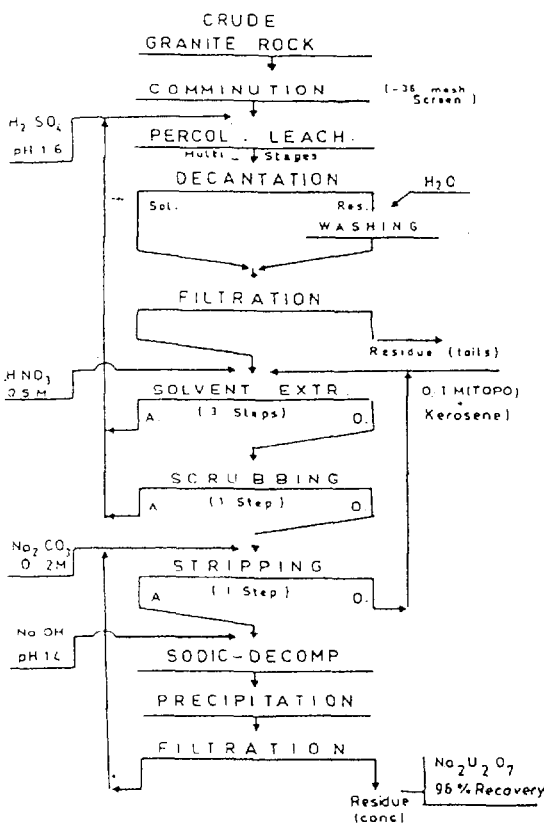


Figure (5) : Proposed Flowsheet for Recovering Uranium From Granite of El-Aradiya, Eastern Desert

Uranium Stripping Circuit: The U value is then stripped from the washed loaded extract in one stage using an aqueous alkaline solution of 0.2 M Na_2CO_3 at an O/A phase ratio of 5:1. The realized uranium concentration in the stripped solution attains about 15.0 gU/L.

Uranium Precipitation Stage: Uranium is precipitated as sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) of about 70% U using NaOH solution at pH 11.0 (i.e. sodic decomposition). The slurry was then subjected to filtration where the filtered product $\text{Na}_2\text{U}_2\text{O}_7$ represents the final product while the filtrate is used for recycle to the stripping step after necessary regeneration and make up.

Conclusion

On the basis of the results of the foregoing studies, the following conclusions could be derived:

1. The percolation leaching technique applied on El Erediya granitic head sample does not require over-grinding, classifying or thickening equipment, and therefore it would effect savings in power and reagents consumptions. In other words capital construction and operational costs can be reduced.
2. Multi-stage percolation leaching process has given reasonable U percent recovery reaching 97% within 6 weeks. Acid consumption was 20 kg/ton when a H_2SO_4 solution of pH 1.4 is used for leaching U from comminuted head sample (-36 mesh). Continuous recycling of the acid leach solution can increase the U concentration greater than 1.2 g/l and would diminish H_2SO_4 consumption to 18 kg/ton.
3. Excellent U extraction % of more than 96% was attained by using 0.1 M TOPO in kerosene at 1/3 O/A phase ratio and 5 minutes mixing time.
4. U is effectively stripped with a recovery percent above 98% from the pregnant organic solvent by using 0.2 M Na_2CO_3 solution, where it reports in the stripping solution in the form of soluble $(\text{UO}_2(\text{CO}_3)_3)^{4-}$. The latter could then be precipitated as $\text{Na}_2\text{U}_2\text{O}_7$ containing 70% U by using sodic decomposition at pH 11.0.

A proposed flowsheet was designed to recover U from El Erediya granite with an overall recovery of 90.15%.

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