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Comparative Study on Precipitation Methods of Yellow-Cake from Acid Leachate of Rock Phosphate and Its Purification

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Dedication

To the soul of my father, my mother, my
brothers and my sisters

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ABSTRACT

This study was carried-out to leach uranium from rock phosphate using sulphuric acid in presences of potassium chlorate as an oxidant and to investigate the relative purity of different forms of yellow cakes produced with ammonia $\{(NH_4)_2 U_2 O_7\}$, magnesia $(UO_3 \cdot xH_2O)$ and sodium hydroxide $(Na_2U_2O_7)$ as precipitants, as well as purification of the products with TBP extraction and matching its impurity levels with specifications of the commercial products.

Alpha-particle spectrometry was used for determination of activity concentration of uranium isotopes (^{234}U and ^{238}U) in rock phosphate, resulting green phosphoric acid solution, and in different forms of the yellow cake from which the equivalent mass concentration of uranium was deduced. Likewise, AAS was used for determination of impurities (Pb, Ni, Cd, Fe, Zn, Mn, and Cu).

On the average, the activity concentration of uranium in the rock phosphate was 1468 ± 979 Bq/Kg (119.38 ± 79.66 ppm), and 711 ± 252 Bq/L (57.85 ± 20.46 ppm) in the resulting green solution with corresponding percent of dissolution amounting to 48% which is considered low indicating that the experimental conditions (i.e. dissolution container, temperature, pH, retention time) were not optimal. However, the isotopic ratio (^{234}U : ^{238}U) in all stages of hydrometallurgical process was not much different from unity indicating lack of fractionation.

Crude yellow cakes (hydrated uranium trioxide, ammonium diuranate and sodium diuranate) were precipitated from the green solutions prior to separation of iron and once after iron separation. Although, iron was tested using bipyridine and SCN^- , it was found in all types of crude samples analyzed this might be attributed to either the quality of the reagent used or inhibition of Fe present in the solution by stronger complexing agent. Uranium mass concentration in crude yellow cakes precipitated before iron separation was found following the order: $UO_3 \cdot xH_2O$ > ammonium diuranate > sodium diuranate. Upon comparing the level of impurities in each type of crude yellow cake precipitated before and after iron separation it was found that their levels were almost identical with $UO_3 \cdot xH_2O$. This implies that saturated magnesia is least aggressive relative to other precipitants and gives relatively pure crude cake. Therefore, it was used as an index to judge the relative purity of other types of yellow

cakes by taking the respective elemental ratios. The levels of impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in the purified yellow cake were found comparable with those specified for commercial products.

الخلاصة

أجريت هذه الدراسة لاستخلاص اليورانيوم من الصخور الفوسفاتية باستخدام حمض الكبريتيك في وجود كلورات البوتاسيوم كعامل مؤكسد ولتَحْرِي النقاوة النسبية للصيغ الكيميائية للوكاز الأصفر المنتج باستخدام محلول الأمونيا $(NH_4)_2 U_2 O_7$ ، محلول أكسيد المغنيسيوم المشبع $(UO_3 \cdot xH_2O)$ ومحلول هيدروكسيد الصوديوم $(Na_2U_2O_7)$ كمرسبات، بالإضافة إلى تنقية المنتجات بالمذيب العضوي ثلاثي بيوتيل الفوسفات ومقارنتها بمستوي الشوائب الموصي به في العينات التجارية من الركام الاصفر.

استخدمت مطيافية الفا لتحديد التركيز الإشعاعي لنظائر اليورانيوم (^{234}U و ^{238}U) في عينات الصخور الفوسفاتية، محلول حمض الفوسفوريك الناتج، والصيغ المختلفة للوكاز الاصفر أُستنتج التركيز الكتلي لليورانيوم بالجزء من المليون في كل العينات المحللة من التركيز الإشعاعي المقاس. بالمثل استخدمت مطيافية الامتصاص الذري لتحديد تركيز عناصر الشوائب (الوصاص، النيكل، الكاديوم، الحديد، الزنك، المنجنيز والنحاس).

في المتوسط وجد ان التركيز الإشعاعي لليورانيوم في الصخر الفوسفاتية هو 979 ± 1468 بكريل / لجم (الوزن الكتلي الموازي 119.38 ± 79.66 جزء من المليون)، و 252 ± 711 بكريل / لتر (الوزن الكتلي الموازي 57.85 ± 20.46 جزء من المليون) في محلول حمض الفوسفوريك الناتج بنسبة اذابة مناظرة تبلغ 48% والتي تعتبر منخفضة مما يدل على أن ظروف التجريب (أي حاويات الاذابة، درجة الحرارة، درجة الحموضة و زمن البقاء) ليست مثالية. ومع ذلك، فإن نسبة النظير ^{234}U الي ^{238}U في جميع مراحل المعالجة الميتالورجية لا تختلف كثيراً عن الواحد مما يدل على عدم وجود تجزئة نظائرية خلال عملية المعالجة.

رسبت الصيغ الكيميائية المختلفة ل لوكاز الاصفر الخام (ثالث أكسيد اليورانيوم المائي، ثنائي يورانيل الصوديوم و ثنائي يورانيل الأمونيوم) من محلول حمض الفسفوريك قبل فصل الحديد وبعد فصل الحديد لمعرفة تأثير الحديد علي عملية فصل اليورانيوم بالمذيبات العضوية في المراحل اللاحقة. على الرغم من اختبار وجود الحديد او عدمه بعد الفصل باستخدام البايبريدين والثايسيانيد إلا انه وجد في جميع أنواع عينات الخام المحللة، يمكن أن يعزى هذا إما إلى جودة الكواشف المستخدمه أو شحيط الحديد في المحلول بمعقد اقوي مما يحول دون تفاعله مع محاليل الاختبار. في الركام الاصفر الخام المرسب قبل فصل الحديد وجد ان تركيز اليورانيوم يتبع

الترتيب التالي : ثلاثي اكسيد اليورانيوم المائي < ثنائي يورانيول الأمونيوم > ثنائي يورانيول الصوديوم. بمقارنة مستوي الشوائب في كل انواع ال ركاز الاصفر الخام المرسب قبل وبعد فصل الحديد وجد ان مستوي الشوائب كان متماثلا تقريباً في ثلاثي اكسيد اليورانيوم المائي . هذا يُشيرُ ضمناً إلى أنّ أكسيد المغنيسيوم الهشيع كعامل مؤكسد أقلّ قساوة مقارنة بالمرسبات الاخرى مما يعطي ركاز خامّ نقي نسبياً. لذا، استعمل كمرجع للحكم علي النقاوة النسبية للصيغ الأخرى من الراكز الأصفر بأخذ النسب العنصرية بها مقابل ثلاثي اكسيد اليورانيوم المائي.

بعد تنقية الركاز الاصفر باستخدام ثلاثي بيوتيل الفوسفات وجد أن مستويات تراكيز عناصر الشوائب (الحديد، الزنك، المنجنيز، النحاس، النيكل، الكاديوم والرصاص) في الركاز النقي لا يختلف كثيراً عن المستويات المرجعية للمنتجات التجارية.

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CHAPTER ONE

INTRODUCTION

1. INTRODUCTION

1.1 Front nuclear cycle:

Following the development of the nuclear industry for peaceful applications to address the issues pertinent to socio-economic welfare of mankind particularly in the field of power generation and isotope production, attention was focused on developing technologies, which could be used to upgrade and purify uranium from low-grade sources. Initially the nuclear industry had relied on high-grade uranium ores. The production of yellow cake was an essential step in this development (Makenzie, 1997). In this study we aim to concentrate uranium from rock phosphates using different precipitants and examine their merits and demerits with respect to impurities.

Uranium is present in the Earth's crust at an average concentration of 2 parts per million. Acidic rocks with high silicate, such as granite, have higher than average concentrations of uranium, while sedimentary and basic rocks have lower than average concentrations. Uraninite or pitchblende (U_3O_8), the most common uranium-containing ores, is mixtures of UO_2 (basic) and UO_3 (amphoteric) oxides. The concentration of U_3O_8 in ores can vary from 0.5% in Australian ores to 20% in Canadian ores. Also uranium is present in sea water, at about 0.003 ppm (IAEA, 1993).

The nuclear fuel cycle is a series of steps that produce fuel for nuclear power reactors, which in turn generate electricity. The nuclear fuel cycle is the complex process of preparing uranium for fuel use in nuclear power reactors (mining and milling, conversion, enrichment, and fuel fabrication); these steps are known as the front end of the fuel cycle. Figure (1.1) shows the block diagram of Uranium processing. The back end of the fuel cycle refers to the storage, reprocessing and disposal of the uranium after its use in the reactor.

Mining is first step in nuclear fuel cycle and it is carried out depending on the ore depth and environmental conditions, through either open pit or underground mining. The open pit mining operations applied to sedimentary and vein type ore bodies and it used for near surface deposits. Open pit mining is preferred to under ground operation because of high productivity and better ore recovery, easier dewatering and safer mining.

However, it has disadvantage of greater environmental impact than underground mining. Safety is very important from radiation hazard come from direct radiation, dust and radon (IAEA, 1993).

The second step of nuclear fuel cycle is milling. This step involves crushing and grinding operation to produce a suitable size for acid or alkaline leaching.

1.2 Uranium leaching chemistry:

Leaching is an important step in the processing of uranium ore. The leaching process controls a) the proportion of uranium solubilised of the ore, b) the quantities of reagent, which are major operating cost, required to maintain suitable leaching condition, c) the concentration of impurities in solution, and d) the grinding requirements.

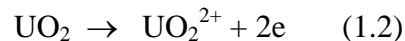
Uranium ores are treated by either acid or alkaline reagents. Several factors must be considered to select acid or alkaline reagent such as carbonate content of the ore, efficiency of uranium extraction, water usage, energy consumption, product quality requirements and environmental consideration (IAEA, 1993). In this study acid leaching is used and the theoretical background of the process will be detailed in subsections below.

1.2.1 Acid leach chemistry for uranium:

There are two valence states in which uranium occur naturally, the hexavalent form, the oxide of which is UO_3 , and tetravalent form, the oxide of which is UO_2 . In hexavalent form uranium goes directly into solution as given by eq.(1.1)



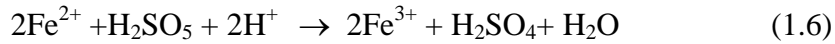
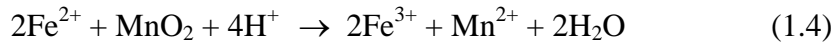
The tetravalent goes into solution after oxidation to hexvalent as shown:



This oxidation can be achieved by ferric in the leach solution as given by this equation:

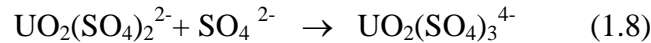
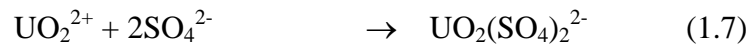


To maintain the dissolution of UO_2 the Fe^{3+} must be renewed by subsequent oxidation of Fe^{2+} formed in eq.(1.3) .If manganese dioxide is used as the oxidant, the following reactions will take place:



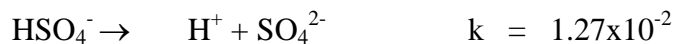
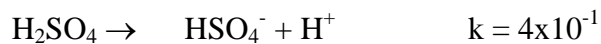
The consumption of acid required to achieve the equivalent oxidation of ferrous is reduced by 50% if sodium chlorate or caro's acid are used instead of pyrolusite as in reaction (1.5) and (1.6), respectively.

By using sulphuric acid in presence of an oxidizing agent which provides a leach oxidation-reduction potentials of 400-500 mV relative to saturated calomel electrode, being present in hexavalence form as uranyl ion this reaction occurs as:



The uranyl sulphate anion complexes are species, which are extracted by solvent. Unfortunately the oxidizing sulphuric acid leach, which is often carried out temperature at 40-80 °C is aggressive and non-selective resulting in many other species besides uranium being leached Makenzie, (1997). The species which present problems in uranium solvent extraction involve: Soluble silica [Si(OH)₄], Amorphous (SiO₂), Tungsten (WO₄)²⁻, Antimony (SbO₄)³⁻, Arsenic (AsO₃)³⁻, Molybdenum (MoO₄)²⁻, Vanadium (VO₃)⁻, Zirconium (ZrO₃)²⁻, Titanium (TiO₃)²⁻, and Phosphate (PO₄)³⁻.

In addition sulphuric acid dissociates in water as follows:



Chloride (Cl⁻) and nitrate (NO₃⁻) anions may also be present in the leach liquor (Makenzie 1997).

1.3 Uranium purification:

A number of methods depending upon type of solution can accomplish the purification of the clarified leaching solution. The variables include (IAEA, 1993):

- a. Concentration of uranium.
- b. The amount and concentration of impurities.
- c. The desired final purity of the uranium product.

The leaching solution composition will essentially be dependent upon the mineralogy of the ore, and leaching medium. Thus, a number of purification combinations may be applicable. For example, the alternative can include the following, depending upon the feed solution analysis and grade of product demanded (IAEA, 1993):

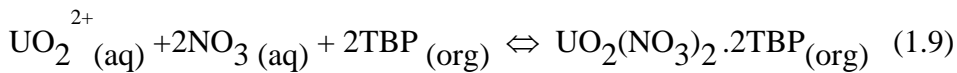
- a. direct precipitation from alkaline and some acid liquors
- b. Ion exchange, elution and precipitation.
- c. Solvent extraction, stripping and precipitation.
- d. Ion exchange followed by solvent extraction.

1.3.1 Solvent extraction:

The recovery of uranium from ores by using solvent extraction (diethyl hexylphosphoric acid (DEHPA)), the DAPEX process, and secondary or tertiary amines (the AMEX process) has been popular extractions. A common organic phosphate tri-n-butyl phosphate (TBP) is widely used for separating uranium (VI) from co-existing elements in a nitric acid medium (IAEA, 1993).

The distribution coefficient is considerably large over an acid range from pH 3-6 M nitric acid and increases with increasing both uranium and nitric acid concentration and reaches a maximum at 5 M HNO₃ Jamal et al., (2005).

The advantage of (TBP) is non-volatile with boiling point of 289 °C, and stable with concentrated nitric acid. The disadvantage that iron, thorium and protactinium are co-extracted with uranium in nitric acid, so if there is one of them, it must be separated prior to extracting uranium. The extraction of UO₂²⁺ by (TBP) from slightly acid medium can be described as:



Due to the large alkyl groups of TBP (C₁₂H₂₇O₄P) the complex compounds are readily soluble in organic solvents (e.g. kerosene). The distribution coefficient for the TBP extraction is given as:

$$D = \frac{[UO_2(NO_3)_2 * 2TBP]}{[UO_2^{2+}]} \quad (1.10)$$

The application of the law of mass action to equation (1.10) gives:

$$K = \frac{[UO_2(NO_3)_2 \cdot 2TBP]_{org}}{[UO_2^{2+}][NO_3^-]^2 [TBP]^2} \quad (1.11)$$

Where, K is the equilibrium constant. Thus, the distribution coefficient finally becomes:

$$D = K [NO_3^-]^2 [TBP]^2 \quad (1.12)$$

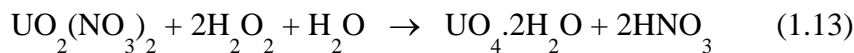
From equation (1.12) the distribution coefficient increases with increasing nitrate content.

Following extraction the loaded solvent is usually contacted with a scrub solution to remove impurities from solvent prior to recovery of uranium Nasser, (2004).

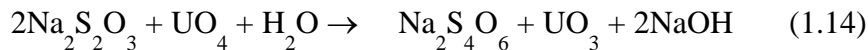
1.3.2 Stripping and precipitation:

After scrubbing, the solvent passes to the stripping circuit where uranium is recovered in aqueous solution by contact of solvent with suitable aqueous solution such as sodium or ammonium carbonate.

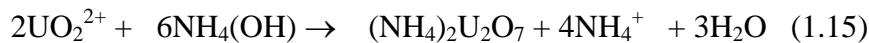
The strip solution is precipitated by ammonia or hydrogen-peroxide to produce yellow cake. The H_2O_2 used for precipitation of uranium peroxide from strip solution after acidification with HNO_3 to pH 3.5 at 70 °C with stirring according to the following reaction:



The UO_4 is converted to UO_3 by heating at 450 °C or by reducing it with $Na_2S_2O_3$ solution as following:



By using ammonium hydroxide the yellow cake is precipitated as ammonium diuranate $(NH_4)_2U_2O_7$, as following:



The product is dried in an oven at 100 °C and then calcined at 350 °C to obtain UO_3 (Nasser, 2004).

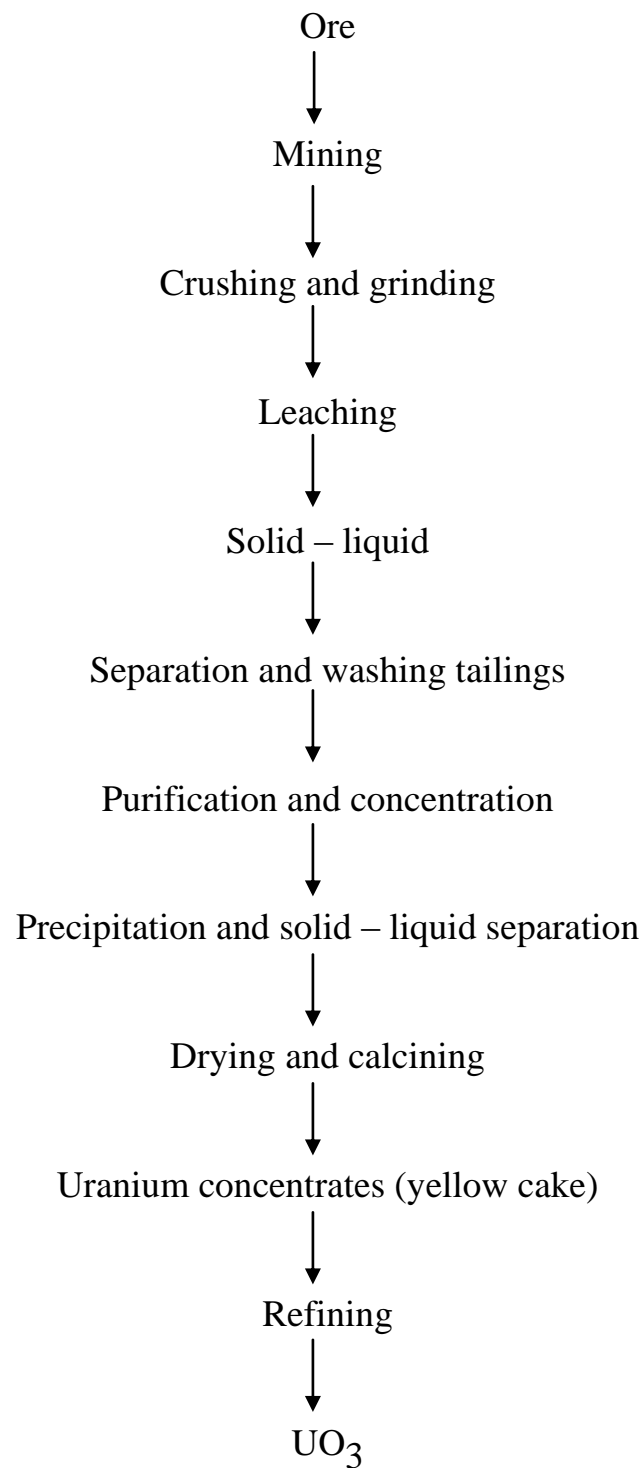


Fig.1.1: Flow diagram of uranium processing

CHAPTER TWO
LITERATURE REVIEW

2. LITERATURE REVIEW

Considerable work had been carried out in uranium mining, milling and processing since last century and people used different techniques and methods to modify and improve purification processes. Maria *et al.*, (1977) used tributylphosphate (100% TBP) as a solvent for separating impurities in uranium yellow cakes. Trace metals are separated and concentrated by solvent extraction from 6M nitric acid into 100% TBP. They found that the efficiency of extraction was 99.9% and the method was fast and economic, and the results were in good agreement with those obtained by specific methods for each element after prior separation of uranium by precipitation or solvent extraction with various solvents.

Faizal *et al.*, (2000) used a mixture of TBP/ kerosene to purify and produce ammonium diuranate (ADU) from rare earth (RE) metals and they recovered 98.75 % of U with yellow cake (ADU) which contained U = 67.55 % and undetected RE_2O_3 . Lee *et al.* (2000) used TBP extraction and anion exchange columns technique for determination of uranium isotopes in highly contaminated soil samples. They found that it was an accurate and reliable technique of uranium isotopes determination and uranium was completely separated from the radionuclides in highly contaminated samples.

Mathur *et al.*,(2000) used biogenic ferric sulfate for extraction of uranium from quartz chlorite-sercite ore and found that an extraction efficiency up to 95% has been obtained. Zil'berman *et al* (2001) used 30% tributylphosphate (TBP) in Dodecanese under conditions of the second organic phase to extract uranium (IV) and uranium (VI) from nitric acid solutions. By comparing extraction for the elements for similar conditions, when using non-stratified extraction system (30% TBP in hexachlorobutadiene), it was shown that during uranium extraction from aqueous phase for both systems noticeable differences were pointed out. Study of absorption spectra of the light and heavy organic phases suggested that solvate forms in both organic phases differ for uranium (IV) and uranium (VI).

Clements *et al.*, (1980) used dilute HCl (0.05 M) for leaching of uranium, vanadium, and phosphorus from phosphate. They found that 93% of uranium was leached within 90 min. Acetone and ammonium fluoride mixture was used by Weterings and Janssen,

(1985) to precipitate uranium from phosphoric acid they found this method was economic. Cynthia and Robert, (1986) used weak acid cation resins to recover uranium from carbonate leach liquors and found that a weak-acid cation system was effective in primary, high level uranium recovery, and ground water restoration. Also they found final product purities exceed by far, those achieved with anion exchange resin especially if the process is used throughout the lifetime of a well site.

Hydrogen peroxide was also used in excess to precipitate uranium from uranyl sulphate solutions and the yields were high and the crystals sculleries exhibited good handling characteristics as indicated by Hopkins *et al.*, (1987). Gupta *et al.* (2004) used hydrogen peroxide to precipitate uranium peroxide from the eluted solution after iron removal at pH of 3.5, they found that uranium peroxide can be effectively precipitated from eluted solution with hydrogen peroxide to obtain 98 –99% U_3O_8 in the final product, with 99.5% recovery under these conditions: precipitation temperature $26^{\circ}C$ (room temperature), amount of H_2O_2 28.6% more than stoichiometric amount precipitation, pH 3.5 precipitation time was 4 hr and drying temperature was $600^{\circ}C$.

Also uranium peroxide (UO_4) precipitation diagrams were constructed by Djogi *et al.* (2005) with direct mixing of uranyl perchlorate and hydrogen peroxide solutions. The concentration boundary was stabilized three days after mixing the uranyl peroxide solutions. From the newly established concentration boundary, the uranium (VI) peroxide solubility product was calculated: $K_{sp} = [UO_2^{2+}]_{free} \times [O_2^{2-}]_{free}$. The mean value of the solubility product (K_{sp}) was found to be $(1.32 \pm 0.02) \times 10^{-36} \text{ mol dm}^{-3}$.

Wisnubroto (1997) used diethyl hexyl phosphoric acid (HDEHP) and Tri-octylamine for U recovery from sulfuric acid solution and he found that the later compound was easier to use, and also has a good selectivity on recovery uranium.

Babain *et al.*, (2001) used gas extraction of actinide complexes with beta-diketones prepared beforehand and analogous ones synthesized in-situ. It was determined that tributylphosphate in supercritical carbon dioxide can extract macro-quantities of uranyl nitrate efficiently. Experiments on preparation of uranyl complexes in-situ showed that in the case of low excesses beta-diketones do not permit to extract uranium from uranyl nitrate. In the same time uranyl carbonate was extracted efficiently by fluorine-containing beta-diketones under the same conditions. Introduction of additional neutral

ligand permits to increase efficiency of extraction. Introduction of pyridine into solutions of beta-diketones in supercritical carbon dioxide leads to increase of uranium extraction efficiency from uranyl nitrate and does not affect on uranyl carbonate extraction. Data obtained confirmed that basic function of pyridine was binding of nitric acid escaping during formation of complexes of beta-diketones.

Thompson (2002) used solvent extraction process to recover uranium and technetium from solutions of irradiated commercial reactor fuel while sending the plutonium to waste with the fission products and higher actinides was tested with actual fuel solution. He found the process meets all goals for recovery and decontamination.

Awwad (2003) used TPPO to extract uranium (VI) from aqueous nitrate medium; it was found that uranium extraction by TPPO was suitable in toluene as diluents than cyclohexane and chloroform. Sodium hydroxide solution is suitable for stripping uranium from TPPO in toluene.

Puget, (2002) used solvent extraction process for treating a wastewater containing dissolved uranium. They used Alumina 336 (a mixture of tri-octyl and tri-decyl amines) as extractant in this process. The result showed that it was possible to reach an efficiency of about 95% for the uranium extraction, for metal concentration in the feed of 10 ppm. Furthermore, an efficiency of about 50% was reached for metal concentration in the feed of 1 ppm when the liquid flow rate was equal 1200 L/h.

Cao *et al.*, (2000) have proposed flow-sheet for obtaining yellow cake from sandstone ores containing uranium to recover uranium in the form of magnesium diuranate (MDU). The amount of calcium carbonate (g CaCO₃ /100g of ore) reacted with HCl under different conditions of temperature and time showed that stirring method requires high acid consumption. The results obtained from static leaching of the 3 ore categories showed that leaching efficiency largely depends on the weathering degree and particle size of ore. The lowest leaching efficiency was observed for non-weathered ore. In order to increase uranium extraction this ore was ground to the size of maximum 2.5 mm, and then incubated by 40% H₂SO₄ for 48 hours with the addition of KClO₃ (3 kg/tonne of ore) as oxidant. The results of acid purging showed that uranium extraction efficiency reached minimum 92%. The leaching experiments were carried out under the following conditions: particle size of ore: weathered: maximum 30 mm,

Semi-weathered: maximum 10 mm, Non-weathered: maximum 2.5 mm (incubated by 40% H₂ SO₄); Temperature 25-30⁰C; redox potential; pH 1.0, acid consumption: 40-50 kg/ore tone. Leaching efficiency reached 90%. Uranium concentration in the solution after 8-stage counter-current leaching was min. 4 g/L, uranium content in solid waste 0.01%. Leaching solution was filtered and directly neutralized through two stages to precipitate yellowcake. Experimental data showed that the uranium recovery reached 90%. Yellow cake product met the relevant specifications and had U₃O₈ content of 76%.

Fyodorov, (2002) used *In Situ* Leaching (ISL) method to produce uranium from open-pit and underground mines; they found this method has a number of economical and ecological advantages. Dung *et al.*, (2002) determined several elements (V, Mo, Fe, Mn, Cd, Zn) as metallic impurities in pure uranium compounds by atomic absorption spectrometry. The effects of uranium and that of other factors on the absorption intensity of each element were studied. The analyzed samples were dissolved in 6 M nitric acid, and uranium was selectively extracted with tributylphosphate. The aqueous solution containing impurities was measured with a flame atomic absorption spectrometer under the optimum conditions; they found the analytical procedure for the determination of these above-mentioned elements in synthesized uranium samples and in purified uranium oxide samples with high precision and accuracy.

Two mathematical models representing the effect of five parameters (uranium, iron, HDEHP concentration, P₂O₅%, and organic/aqueous ratio) was established by Stas *et al.*, (2002) on selectivity and yield of U(VI) extraction, allowing the choice of the desired experimental condition and estimation of the purity of the loaded solvent (U_{org}/Fe_{org}). They found that factors that increase the selectivity decrease the yield and vice versa.

The synergistic extractant di-nonyl phenyl phosphoric acid (DNPPA) and tri-n-butyl phosphate (TBP) was used for recovery of uranium from weak phosphoric acid by Singh *et al.*, (2004). They found that solvent was stable and stripping with concentrated phosphoric acid under reducing conditions is efficient, and high-purity uranium was recovered from the strip solution by a second cycle of extraction with D2EHPA-TBP where in a scrubbing step has been incorporated and stripping was performed by an alkaline solution.

El-Hazek and El-Sayed (2003) have proposed a new liquid emulsion membrane (LEM) process for uranium extraction from either dehydrate 28-30% P_2O_5 (DH) or hemi-dihydrate 42-45% P_2O_5 (HDH) wet process phosphoric acid. In this process, the organic component of the LEM was composed of a synergistic mixture of 0.1M di-2-ethyl hexyl phosphoric acid (DEHPA) and 0.025M trioctyl phosphine oxide (TOPO) with 4% sorbitol anhydride monooleate (Span 80). The internal or the strip acid phase was composed of 0.5M citric acid. The prepared LEM was proved to be stable in 42-45% P_2O_5 acid concentration range and can, therefore, be applied to the phosphoric acid produced by the hemi-dihydrate process. After breakdown of the loaded emulsion, the uranyl citrate in the internal strip phase is separated by adding methanol followed by its calcination to the orange oxide. Most of the reagents used were recycled. The proposed process was characterized by simplicity, practically closed operation cycle in addition to lower capital and operating costs.

Mohammed and Eltayeb, (2003) used 25% TBP in kerosene to extract uranium from Uro phosphate ore. For this purpose first, the phosphate ore samples have been leached with concentrated sulphuric acid. The resulting phosphoric acid has been filtered off, and pretreated with pyrite and activated charcoal. The chemical analysis of the obtained green phosphoric acid solution showed that about 98% of uranium content of the phosphate ore was rendered soluble in the phosphoric acid. A three stage extraction at a phase ratio (aqueous/organic) of 1:2, followed by two stages stripping using 0.5 M sodium carbonate solution at a phase ratio (A/O) of 1:4 have been found to be the optimum conditions to report more than 98% of uranium content in green phosphoric acid to the aqueous phase as uranyl tricarbonate complex ($UO_2 (CO_3)_3$). By applying decomposition upon the stripping carbonate solution using 50% sodium hydroxide, about 98% of uranium content was precipitated as sodium diuranate concentrate ($Na_2U_2O_7$). The chemical analysis using atomic absorption spectrometry (AAS) showed a good agreement between the specifications of the obtained uranium concentrate with the standard commercial specification of sodium diuranate concentrate. Further purification was achieved for the yellow cake by selective precipitation of uranium from the solution as uranium peroxide ($UO_4 \cdot 2H_2O$) using 30% hydrogen peroxide. Finally the uranium peroxide precipitate was calcined at $450^{\circ}C$ to obtain the orange powder uranium trioxide (UO_3). The chemical analysis of the final uranium trioxide product has proved its nuclear purity and meets the standard commercial specification. According to

the obtained results, it can be concluded that nuclear grade uranium trioxide can be successfully produced with an overall uranium recovery percentage of 93% from Uro phosphate ore.

El-Kamash *et al.*, (2002) used extraction chromatography to study the extraction of both U(VI) and U(IV) from nitric acid solutions using TBP solvent impregnated polyacrylic acid polymer (SM-7) as inert supporting material. Batch kinetic and breakthrough column experiments were carried out to explain the mechanistic aspects of the extraction process obtain thermodynamic parameters and simulate its applications. Based on the experimental results, an approximate and simplified first order kinetic expression has been used to interpret the metal depletion in the liquid phase. A mathematical model, consists of metal ion mass transfer and column mass balance equations, was proposed to predict the breakthrough curves of both metal ions on an extraction column. The predicted breakthrough curves were in a good agreement with the experimental data. These results suggested that the proposed models are applicable to the interpretation of kinetic data, the prediction of breakthrough curves can be used as a design tool for extraction chromatographic process.

Nazari *et al.*, (2003) used polyalkyl phosphazenes (PN-1200) for extraction of uranium from wet process phosphoric acid and they found that it has good uranium distribution coefficient, good stability, good phase separation, acceptable kinetics and simultaneous extraction of U^{4+} and U^{6+} .

Immobilized and dried powdered *Trametes versicolor* and *Phanerochaete chrysosporium* basidio spores were used by Genç *et al.*, (2003) for the recovery of uranium from aqueous solutions. The biosorption of UO_2^{2+} ions on carboxymethylcellulose and immobilized and heat-killed fungal mycelia of *T. versicolor* and *P. chrysosporium* was studied from aqueous solutions in the concentration range of 100–1000 mg/l. The biosorption of UO_2^{2+} ions by the carboxymethylcellulose and immobilized and dried powdered preparations increased as the initial concentration of uranium ions increased in the medium. Maximum biosorption capacities for immobilized and dried powdered fungal mycelia of *T. versicolor* and *P. chrysosporium* was found as 309.1 mg UO_2^{2+} /g and 158.0 mg UO_2^{2+} /g, respectively; whereas the amount of UO_2^{2+} ions adsorbed on the plain carboxymethylcellulose beads was 29.2 mg/g. The effect of pH was also investigated

and the maximum adsorption of UO_2^{2+} ions on the carboxymethylcellulose and both live and heat-inactivated immobilized fungal mycelia were observed at pH 4.5.

Kütahyalı and Eral (2004) used activated carbon prepared from charcoal by chemical activation for adsorption of uranium from liquid aqueous radioactive wastes. The adsorption of uranium was studied as a function of pH, concentration of adsorbate, shaking time, particle size, amount of adsorbent and temperature. The uranium adsorption efficiency was found as $92\pm 4\%$.

Krestou *et al.*, (2004) studied hydroxyapatite (HAP), $\text{Ca}_5\text{OH}(\text{PO}_4)_3$, as a mechanism for the removal of hexavalent uranium from water. The work showed that the attenuation mechanism of HAP can be attributed to bulk precipitation with almost 95% removal of U(VI) in a very short time, regardless of the applied conditions. A theoretical study of the HAP-U(VI) system showed that, depending on the pH, uranium (VI) can be precipitated either in the form of $\text{Ca}(\text{UO}_2)(\text{PO}_4)_2$ or as $\text{CaUO}_2(\text{CO}_3)_2$. The precipitates formed are extremely stable in acid and neutral solutions, but not in alkaline solutions where an amount of $\approx 32\%$ of the precipitated uranium (VI) is dissolved.

El-Nadi and Daoud (2004) used pure and commercial sodium sulphide for precipitation of Fe (III) from phosphoric acid medium, they found that it was useful for precipitation of Fe (III) and the pure form gave better results compared with the commercial one. Ten minutes were found to be quite sufficient for complete precipitation and the temperature increases the precipitation percent. The synergic mixture of diethyl hexyl phosphoric acid (HDEHP) and CYANEX 921 in kerosene used for the extraction of U(VI) from phosphoric acid showed poor extraction of Fe(III). The extraction of U (VI) from phosphoric acid by HDEHP – CYANEX 921 mixture in the ratio 4:1 decreased with temperature. Also application of the proposed precipitation method for removal of Fe (III) on a commercial green phosphoric acid gave satisfactory results.

Mohamed and Hussein (2004) have applied the microemulsion liquid membrane for extraction of uranium from phosphoric acid produced at Annaba plant in Algeria. They observed that an extraction yield of more than 90% of uranium present in the phosphoric acid may be reached in three theoretical stages with aqueous/organic phase ratio of 12:1 without acid pretreatment for the removal of organic matter.

Atia, (2005) used chitosan/amine and chitosan/azole resins for the uptake of Hg^{2+} and UO_2^{2+} from their aqueous solutions. The chitosan/amine resin showed higher uptake towards Hg^{2+} and UO_2^{2+} compared to chitosan/azole. Selective separation of Hg^{2+} from UO_2^{2+} was achieved at $\text{pH} < 2$. This was explained by the ability of Hg^{2+} to adsorb on chitosan resin through ion-exchange in the acidic media while UO_2^{2+} would not. Uptake values up to 2.0 and 1.7 mmol/g were reported for Hg^{2+} and UO_2^{2+} , respectively, on chitosan/amine. Application of the Langmuir model to the adsorption data indicated a higher binding of Hg^{2+} to the resin compared to UO_2^{2+} . The adsorbed Hg^{2+} or UO_2^{2+} on the studied resins was eluted using H_2SO_4 and HCl , respectively.

Ladeira and Morais, (2005) studied recovery of uranium from nuclear industrial effluent using laboratory column and polymeric ion exchange resin. Uranium is in the form of uranyl quadrivalent complex anions $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. The resin IRA 910 U was employed for its specific application for uranium extraction. Adsorption was carried out at flow rate of 1.0, 2.0, and 5.0 mL/min, which corresponds to a retention time of 10, 5.0 and 2.5 min, respectively. The use of ion exchange technique makes the recovery of more than 98% of the uranium possible. Elution was carried out with ammonium carbonate solutions and also with the diluted effluent.

Nasser and Adam (2005) used concentrated sulfuric acid with and without addition of KClO_3 as an oxidant to leach uranium from rock phosphate deposits in Uro and Kurun at eastern part of Nuba Mountains. They precipitated crude yellow cake from resulting green solution of phosphoric acid as $\text{Na}_2\text{U}_2\text{O}_7$ and $(\text{NH})_2\text{U}_2\text{O}_7$ and subsequently purified by tributylphosphate (TBP) extraction and hydrogen peroxide as $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. TBP purified product was dried and calcined to UO_3 ; whereas $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ dried and reduced to UO_3 by $\text{Na}_2\text{S}_2\text{O}_3$. They found percentage of uranium as U_3O_8 53% in the first one and 38% on the other hand uranium stripping by $(\text{NH}_4)_2\text{SO}_4$ was investigated in order to substitute the NaCl used in the production of uranium concentrate by Morais and Gomiero (2005). The $(\text{NH}_4)_2\text{SO}_4$ concentration, the equilibrium pH effect and the presence of chloride ion in the loaded organic phase were investigated. It was observed that the presence of chloride ion in the loaded organic phase makes the $(\text{NH}_4)_2\text{SO}_4$ stripping process unfeasible. In this case, only 65% of the uranium was stripped. In the absence of chloride, it was possible to obtain a pregnant strip solution with 33 g/L U_3O_8 and an unloaded organic solution with 0.006 g/L U_3O_8 using five mixer-settler stages.

On other hand Morais *et al.* (2005) employed H_2SO_4 solution for stripping uranium from loaded tertiary amine (Alamine-336), which can exceed 100 g/L U_3O_8 . Authors found that there was a low uranium co-precipitation and the sulfate removal was quite efficient, and uranium peroxide precipitation from the pregnant strip solution after sulfate content reduction with a high purity (99.7% U_3O_8) was obtained.

A mixture of sodium carbonate, sodium hydroxide, and hydrogen peroxide was used by El-Nadi *et al* (2005) to separate the hydrous oxide cake containing uranium, thorium, and rare earth elements from the phosphate matrix. It was found that uranium can be selectively leached leaving thorium and rare earth elements as insoluble hydrous oxides. The factors affecting the extraction of uranium from the alkaline solution containing sodium carbonate and hydrogen peroxide were separately studied. Experimental results showed that tricarbonate uranium complexes are selectively extracted by Aliquat-336 diluted in kerosene from alkaline leach solution. Based on these results, uranium was purified from the leach solutions by extraction with Aliquat-336 diluted in kerosene with purity not less than 99%.

A liquid surfactant membrane process for separating U(VI) from sulfuric acid media was investigated using N-alkylcaprolactam (B_5) as a carrier by Yang *et al.* (2005). They found that the liquid membrane containing n-dodecane used as a solvent, ECA4360J as a surfactant and B_5 as a carrier is an effective membrane for extracting U (VI) from sulfuric acid.

Jamal *et al.*, (2005) studied uranium extraction from nitric acid solutions and they found that uranium extraction from nitric acid solutions was fast, and increases with increasing both uranium and nitric acid concentration and reaches a maximum at 5 M HNO_3 . The viscosity of the organic phase increases slightly with increasing uranium concentration in the organic phase. The equilibrium constant of uranium extraction was found to be 102.464 and 102.668 L/mol for 0.5M and 1.0M nitric acid concentrations. Temperature has a negative effect on uranium extraction process, the H° of the extraction reaction was found to be -18.78 and -26.64 kJ/mol for 0.5 M and 1.0 M nitric acid concentrations, respectively and two stages are enough to extract more than 98% of uranium at 5.75 M nitric acid concentration using 0.363 and 0.726 M TBP/kerosene operating lines ($V_{\text{org}}/V_{\text{aq}} = 1/6$ and $1/3$) respectively.

Vijayalakshmi *et al.*, (2005) applied di-nonyl phenyl phosphoric acid in combination with synergistic reagent tri-n-butyl phosphate for separation of uranium from weak phosphoric acid. They reached uranium recovery of 80%.

Cloud-point extraction (CPE) was used with lipophilic chelating agent to extract uranium (VI) from aqueous solutions by *Favre-Re'guillon et al.*, (2006). The methodology used was based on the formation of metal complexes soluble in a micellar phase of a non-ionic surfactant, Triton X-114. The metal ions complexes were then extracted into the surfactant-rich phase at a temperature above the cloud-point temperature. The influence of surfactant concentration on extraction efficiency was studied and the advantage of adding 8-hydroxyquinoline (8HQ) as lipophilic chelating agent was evident. High extraction efficiency was observed, indicating the feasibility of extracting U(VI) using CPE.

Singh *et al.*, (2006) used oxalic acid for the stripping of iron from the extract obtained during second cycle extraction of uranium from phosphoric acid, they found that the resulting extract yellow cake exceeding the specification of commercial grade.

Saxena *et al.*, (2007) used Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for determination of V, Cr, Ni, Co, Cu, As, Ce, Nd, Sm, Eu, Gd, Dy, Pb, U, Zn, Mo, Sr, Y, Cd, La and Th in Wet Phosphoric Acid (WPA) and used charcoal to remove organic material they found that charcoal treatment did not result in any significant change in the concentration of trace elements determined.

Adsorption of U(VI) from aqueous solutions using artificial adsorbents based on magnesia was studied by Gasser (2007). The effect of different parameters affecting the adsorption of this metal ion was investigated. Comparison between the loading capacity of the prepared adsorbents (MF-1, MF-2) for U(VI) was investigated. It was found that the loading capacity of MF-1 was 26 mg/g after four adsorption stages and the capacity of MF-2 was 171.6 mg/g after only one adsorption stage. The studies showed that the capacity of MF-2 adsorbent for removal of U(VI) higher than MF-1. Therefore, the feasibility for pre-concentration of these metals for MF-2 is also reported. It was found that after adsorption of the metal ion on MF-2, the metals ion concentration in the stripping solutions recovered was concentrated 366 times for U(VI) than in the initial concentration.

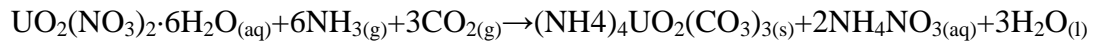
Ho and Quan (2007) investigated the oxidation of iron(II) to iron(III) using an SO₂/O₂ gas mixture in order to provide an iron(III) stream for uranium extraction. The effects of pH, temperature and SO₂/O₂ volumetric ratios were considered. Oxidation of iron (II) by SO₂/O₂ was controlled by diffusion of SO₂ or O₂ at pH 2 and 40 °C. However as the pH decreased below pH 1, the reaction was controlled by a slow chemical step and the reaction rate decreased. Increasing the temperature increased the oxidation rate at pH 0.8, and at 70 °C the rate again became dependent on SO₂ or O₂ diffusion. They found that the uranium extraction achieved with iron (III) solution prepared by SO₂/O₂ oxidation was the same as that for a standard uranium leach with conventional oxidant.

Tri-n-octyl phosphine oxide (TOPO)/n-dodecane was used as a carrier and ammonium carbonate as a receiving phase by Singh *et al.* (2007) for the separation of uranium (VI) from the phosphoric acid medium. Throughout the study PTFE (poly-tetra- fluoro-ethylene) membranes were used as a support. The studies involve the investigation of process controlling parameters like feed acidity of phosphoric acid, carrier concentration and stripping agents. The effect of nitric acid and sodium nitrate in feed was also studied. It was found that there was negligible transport of uranium (VI) from pure phosphoric acid medium but it increases to very significant amount if 2 M nitric acid was added to feed phase. More than 90% uranium (VI) was recovered in 360 min using 0.5MTOPO/n dodecane as carrier and 1.89M ammonium carbonate as stripping phase from the mixture of 0.001 M H₃PO₄ and 2 M of HNO₃ as a feed. The flux and permeability coefficient were found to be 9.21×10^{-6} mol/m² s and 18.26×10^{-5} m/s, respectively. Lower concentration of phosphoric acid with 2M HNO₃ and higher concentration of carrier was found to be the most suitable condition for maximum transport of uranium (VI) from its low-level sources like commercial phosphoric acid.

Kazem and Mahshid (2007) reported an improved process for the separation of uranium from the leached pulp of low grade uranium ore using the resin in-pulp method. They concluded that four stage counter-current resin in-pulp operations under optimum conditions were sufficient to recover about 99% of the uranium from the leached ore.

Mellah (2007) studied the precipitation of ammonium uranyl carbonate (AUC) thermodynamic and kinetic investigations to determine the predominant chemical reaction during precipitation of ammonium uranyl carbonate (AUC) based on thermodynamic analysis and to investigate its kinetics. Four chemical reactions were

considered. The Gibbs free energies, $\Delta rG^\circ(T)$ derived from the Ulich calculations as a function of temperature have been determined between 293.15 K and 353.15 K. The predominant chemical reaction of AUC precipitation was:



According to the AUC precipitation kinetics results, the reaction best fits a second order rate equation. The rate constants k_2 were calculated at 313.15 K and 330.15 K and the activation energy E_a determined using the Arrhenius equation was found as 17.4 kJ/mol.

The effect of the ultrasound on leaching uranium in nitric acid and sulphuric acid media was studied by Avvaru *et al.*, (2008). They found that the leaching rate in the presence of ultrasound was higher with low leach acid concentration of nitric acid (HNO_3), and it was high at high leach acid concentration in the case of sulphuric acid (H_2SO_4) being used as a leachant, when compared to conventional mechanical agitation.

Lottering *et al.*, (2008) used sulphuric acid for leaching uranium from low grade uranium ores in the Vaal River region (South African). They found that dissolutions higher than 90% are very difficult to achieve under the normal operating conditions.

Donat (2009) has studied the removal of uranium (VI) from aqueous solutions onto natural sepiolite by using a batch adsorber. The parameters that affect the uranium (VI) sorption, such as contact time, solution pH, initial uranium (VI) concentration, and temperature, have been investigated and optimized conditions determined. Equilibrium isotherm studies were used to evaluate the maximum sorption capacity of sepiolite and experimental results showed this to be 34.61 mg/g. The experimental results were correlated reasonably well by the Langmuir adsorption isotherm and the isotherm parameters were calculated. The results suggested that sepiolite was suitable as sorbent material for recovery and adsorption of uranium (VI) ions from aqueous solutions.

Uranium (VI) and europium (III) transports across the supported liquid membrane (SLM) had been studied by Joshi *et al.*, (2009) to understand the chemical conditions that affect the selective preconcentration of U(VI) from phosphoric acid feed. The SLM was prepared by impregnating the PTFE microporous membrane with an organic phase consisting of di (2-ethyl) hexylphosphoric acid (D2EHPA) and a neutral organophosphorous oxodonor (tri-n-butyl phosphate (TBP), di-butyl butyl phosphonate

(DBBP), tri-n-octyl phosphine oxide (TOPO), and Cyanex 923) dissolved in n-dodecane. They suggested that the SLM formed by tri-n-octyl phosphine oxide with D2EHPA is best suited for U(VI) transport from phosphoric acid feed with a good selectivity over Eu(III). However, the increase in feed acidity (6 mol/L H₃PO₄) found to retard the transport rate of U(VI) across SLM.

Misra *et al.*, (2009) used micellar-enhanced ultrafiltration technique (MEUF) for the simultaneous removal of dissolved organic namely di-butyl phosphate (DBP) and tri-butyl phosphate (TBP) as well as uranyl ions from aqueous solutions. Throughout the study sodium dodecyl sulphate (SDS), an anionic surfactant was used. The 47 mm diameter millipore ultrafiltration membranes of 3000, 5000 and 10,000 MWCO pore sizes were used and the pressure of the ultrafiltration cell was kept at 1.7 bar for all the experiments. They found that the technique can be effectively employed for the simultaneous removal of dissolved organic (DBP and TBP) and metal ions (uranium) from the aqueous effluent streams.

Donia *et al.*, (2009) used glycidyl methacrylate chelating resins to study the uptake behaviour towards U(VI) in aqueous solutions using batch and column techniques at different experimental conditions. Glycidyl methacrylate chelating resins were obtained through copolymerization of glycidyl methacrylate (GMA) with divinylbenzene (DVB) in the absence and presence of magnetite particles to give GMA/DVB (RI) and GMA/DVB-magnetite (RI-mag), respectively. RI and RI-mag resins were treated with tetraethylenepentamine to give RIa and RIa-mag resins. They found that the maximum uptake capacities obtained at 25 °C were 0.82 and 1.68 mmol/g for RIa and RIa-mag, respectively.

Ten fungal strains were used by Mishra *et al.* (2009) for *in situ* leaching of mainly oxide low grade uranium ore of Turamdih mine. They found that maximum recovery of 71% uranium was obtained with the strain *Cladosporium oxysporum*. The other two strains belonging to *Aspergillus flavus* and *Curvularia clavata* gave 59% and 50% of metal recovery respectively from the same ore.

Singh *et al.*, (2009a) used the synergistic mixture of 0.90 M PC88A+0.15 M TBP as extractant system and 0.5 M (NH₄)₂CO₃ as strippant to recover uranium from a conditioned wet process phosphoric acid. They recovered around 80%. On the other

hand, Singh *et al.* (2009b) studied extraction of uranium using *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) in a low-grade Indian silicate-apatite uranium ore. Parameters such as particle size of the ore, pulp density, and pH of lixiviant media were optimised. They found that the recovery reach up to 96% at the pulp density (PD) of 10% (w/v) and 20% (w/v) with the particles of <76 μm size in 40 days at 2.0 pH and 35 $^{\circ}\text{C}$ temperature and increase to 98% at 1.7 pH and 20% (w/v) pulp density (PD), with a rise in redox potential from 595 mV to 715 mV in 40 days.

CHAPTER THREE
MATERIAL AND METHOD

3. MATERIAL AND METHOD

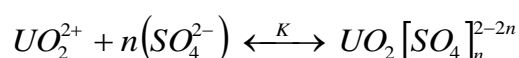
3.1 Sample collection and preparation:

Rock phosphate samples were collected from Uro and Kurun rock phosphate deposits located in eastern part of the Nuba Mountains, Southern Kurdufan State. The information and details of geological and scintillometer mapping are given in Sudan industrial minerals and rocks Mageed, (1998).

The samples were crushed and ground to suitable size (2mm) for leaching. Sub-samples were taken from bulk samples using quartering technique, which consist of piling the ore into conical heap, spreading this out into circular cakes, dividing the cake into quarters, taking opposite quarters as sample and rejecting the other two. The process was repeated until a sufficiently suitable sample of about 3.0 Kg is obtained, then placed in plastic container.

3.2 Acid leaching of uranium:

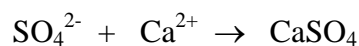
2.5 Kg of the ground homogenized phosphate rocks powder was weighed and placed into a plastic container and 2.5 L of conc. H_2SO_4 was added to it and mixed to be slurry. 7.5 g of potassium chlorate was added as an oxidant to improve the dissolution of uranium. The mixture was left in sun light ($40\text{ }^\circ\text{C}$) for 3 hours with frequent stirring until the reaction was seized and then left for 24 hours at room temperature. 4 liters of deionized water was added and mixed and left in sun light for 3 hours and placed at room temperature for 24 hours. 2 liters of phosphoric acid (green solution) was separated by decantation flowed by centrifugation and the residue was diluted by deionized water, mixed and the resultant green solution was separated. The process was repeated till all green solution was separated. The green solution was mixed with activated charcoal (10 g/L) in order to remove all the suspended organic material and then was filtered using filter papers (125 mm.Ø). 50 ml was saved for analysis and the rest was proceeded with for uranium precipitation. Uranium exits in the leachate as uranyl sulphate complexes:



The most dominant of which is uranyl trisulphate complex $[UO_2 (SO_4)_3]^{4-}$.

3.3 Separation of iron:

Iron and other impurities such as basic sulphates and hydroxides were precipitated from green solution by addition of saturated MgO solution (250g/l) and mixed till pH 3.5. The solution was kept over night and the resulting precipitates of calcium sulphate (gypsum) and iron-gypsum were separated by decantation followed by centrifugation using centrifuge device Model C412 (3000 rpm for 15 mints). The resultant green solution was tested for the presence of Fe by adding one drop of 2,2'-bipyridine (10 mg/ml in ethanol), and SCN⁻ separately to small amount of it in a test tube. Colorless with both reagents indicates the absence of Fe. The iron free solution was used for precipitation of uranium.



3.4 Precipitation of crude yellow cake:

Uranium was precipitated from the green phosphoric acid solution before and after separation of iron as crude yellow cake using three different precipitants, namely NaOH, NH₄OH and MgO. Figure (3.1) shows the experimental design used in block diagram.

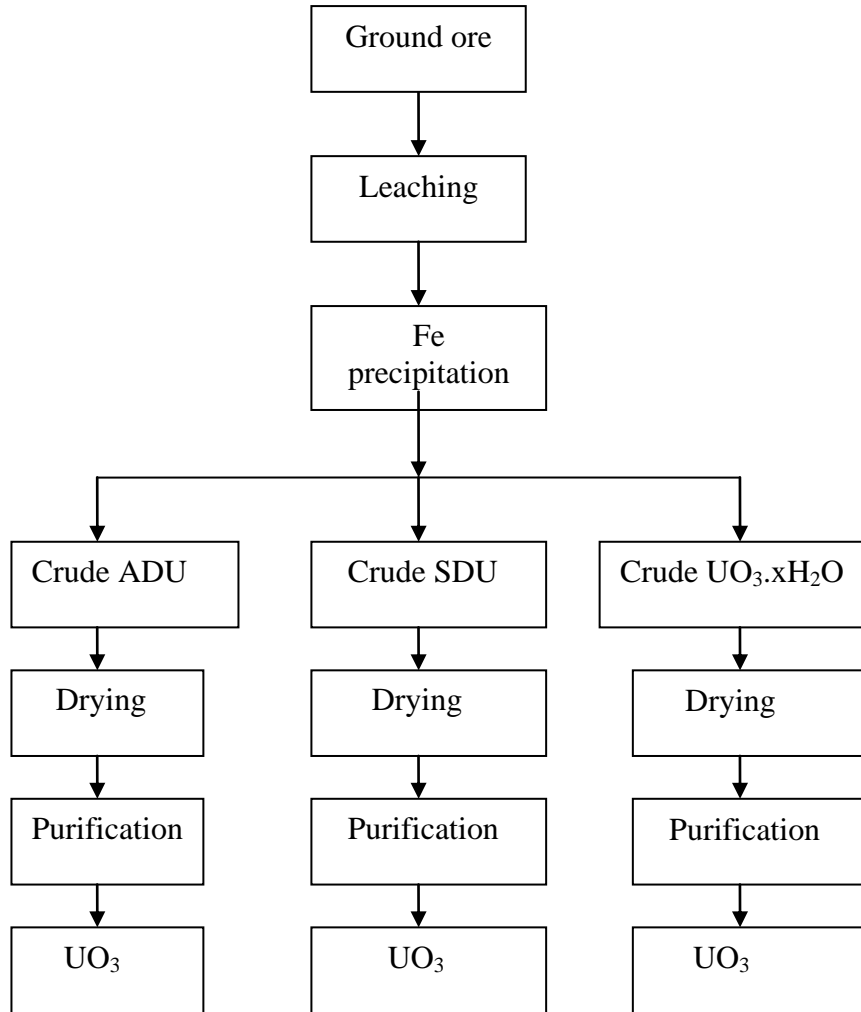
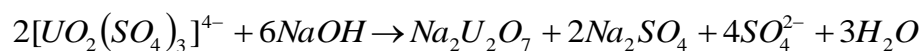


Fig. (3.1):Experimental design of uranium extraction from rock phosphate in block diagram

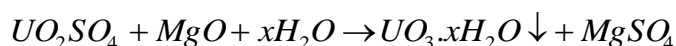
3.4.1 Precipitation of sodium diuranate (Na₂U₂O₇):

Four liters of green solution was used at a time to precipitate uranium as sodium diuranate (SDU). 30% NaOH was gradually added with subsequent stirring until pH 12 was attained. The solution was left over night at room temperature to settle. The precipitate was separated by decantation flowed by centrifugation, washed with deionized water, dried in an oven at 105 °C, and saved as SDU. The balanced reaction can be written as:



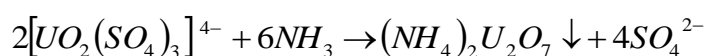
3.4.2 Precipitation of uranium trioxide (UO₃.xH₂O):

Saturated solution of MgO (250 g/l) was gradually added to 4L of green solution with subsequent stirring till pH 7.5. The solution was left over night and the precipitate was separated by decantation followed by centrifugation. It was washed with deionized water, dried in an oven at 105 °C, and saved as UO₃.xH₂O. The reaction is:



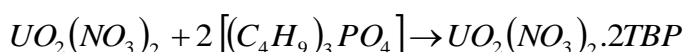
3.4.3 Precipitation of ammonium diuranate [(NH₄)₂U₂O₇]:

One liter of green solution was placed into 2L beaker and stirred with the aid of magnetic stirrer on a hot plate until the temperature of the solution raised to 70 °C, and then 25% ammonia solution was added drop-wise till pH 7.5. The solution was left to cool at room temperature over night and the resultant precipitate was separated by decantation followed by centrifugation. The precipitate was washed with deionized water several times and dried in an oven at 105 °C. The procedure was repeated several times with one liter of green solution. The dried ammonium diuranate was saved as ADU. The reaction can be written as follows:



3.5 Purification of yellow cake:

Different weights ranging from ~30 to 40 g of crude yellow cake were precipitated with different precipitants, digested with concentrated nitric acid and evaporated to near dryness on hotplate. The solution was transferred into a 250 ml separating funnel and the uranium was quantitatively extracted with four portions (75 ml each) of 5% TBP in Kerosene (Aqu./Org. = 2:1). Uranium was recovered from the loaded organic phase with three portions (25 ml each) of 0.5 M Na₂CO₃ (Aqu./Org. = 1:3). Carbonates were destroyed with drop wise addition of concentrated H₂SO₄ to the stripped uranium solution on a hot plate with continuous stirring using magnetic stirrer. The purified yellow cake was precipitated in a form of (NH₄)₂U₂O₇ by drop-wise addition of 10% ammonium hydroxide solution with continuous mixing. (NH₄)₂U₂O₇ was separated by decantation and centrifugation, dried in an oven at 100 °C, and calcined at 350 °C for 6 hours to obtain UO₃.



3.6 Uranium analysis by alpha-particle spectrometry:

3.6.1 Sample preparation:

Known amounts of sample of powdered ore (~ 0.1 – 0.2 g), green solution (1.0 ml), crude and purified yellow cakes (~ 0.1 – 0.2 g) were placed into 250 ml Teflon beakers (triplicate samples). About 0.4 g of ^{232}U tracer solution was added to each sample as a yield determinant. 3ml of concentrated nitric acid was added to immerse the sample and the beaker was covered with watch glass and evaporated on hotplate to near dryness. 5 ml of concentrated hydrochloric acid and 5 ml 40% HF were added to the ore and yellow cake samples. 5 ml concentrated hydrochloric acid was added to the sample of green solution. The samples were heated on hotplate to near dryness. The residues were dissolved in 10 ml 8M nitric acid and made ready for uranium extraction.

3.6.2 Extraction of uranium:

The sample solution was filtered directly into 250 ml separatory funnel and the beaker was rinsed with 10 ml 8M nitric acid twice and 5 ml of tributylphosphate (TBP) $\text{C}_{12}\text{H}_{27}\text{O}_4\text{P}$ was added and shaken for 2 minutes. Each time the aqueous phase was stripped and the organic phase was used for uranium analysis. 15 ml of deionized water was added to organic phase (TBP) in separatory funnel, shaken for 2 minutes and the aqueous phase was stripped and transferred to beaker and acidified with few drops of concentrated hydrochloric acid. The back extraction procedure was repeated once more with 15 ml of deionized water, the aqueous phase collected in the same beaker and evaporated to near dryness. This fraction is now ready for electrodeposition.

3.6.3 Electrodeposition of uranium:

An electropolished stainless steel disc was fitted in the cap of 20 ml polyethylene scintillation vial. The bottom of the vial has been cut off and a hole was drilled through center of the cap for electrical connection to the cathode (disc). The disc which has an exposed area of 2.3 cm^2 , was rinsed with acetone and deionized water prior to be used. The assembly was checked for leakage by filling it with deionized water and leaving it standing for some time on tissue paper. The anode, platinum spiral, was introduced through the bottom of the vial and fitted around 5-mm from the cathode, the solution was not stirred during electrolysis.

1 ml of 0.3 M Na_2SO_4 was added to the uranium solution from above extraction step and completely dried on hotplate, 300 μl of H_2SO_4 was added to the residue and the beaker was warmed and the solution was swirled and residue completely dissolved. 4.0 ml deionized water and 2 drops of 0.2% thymolblue indicator were added to the solution and titrated against concentrated ammonia drop-wise until a yellow/orange endpoint. The solution was transferred to the electroplating cell mounted with stainless steel disc after pretesting the cell stainless steel disc interface for possible leaks and the beaker was rinsed with 5ml 1% H_2SO_4 . The pH of the solution was adjusted to fall within the range (2.1-2.4) with drops of ammonia, or if the endpoint is over stepped, 20% H_2SO_4 acid was added drop-wise to achieve the pH required in the plating solution (the range given above refer to Spezialind Kator pH 0-2.5).

The uranium was electroplated at a current of 1A for 1 hour, at the end of the hour the electrolyte was quenched with 1ml ammonia solution (10 ml concentrated ammonia in 1 liter deionized water) and then with acetone. The end of the disc was touched with tissue paper to absorb the film of acetone and then dried on a hotplate covered with aluminum foil.

Completely dry step mentioned above is essential, since the effectively disposes of nitric acid and hydrochloric acid left from the proceeding sample preparation. Na_2SO_4 serves a carrier during this procedure preventing the actinide atoms from being absorbed onto walls of the beaker.

3.6.4 Quantitative analysis of uranium spectrum:

The α -particle spectra of uranium obtained using ^{232}U as a tracer is shown in Fig.(3.2). Peaks representing the α -energies of different uranium isotopes and their half-lives are given in Table (3.1). For quantitative analysis, the count rates for the constituent radionuclides were obtained by integrating the counts under each peak (Sam, 1998).

The peaks of ^{238}U , ^{235}U , ^{234}U are well resolved and need no correction except background subtraction. However, the shorter-lived nuclide ^{228}Th interfere with peak of ^{232}U . The count rate correction for this interference was performed. 29% of the ^{228}Th group lies under the ^{232}U peak and the 71% branch of the ^{228}Th (5.42 MeV) peak receives the 5% component of its daughter ^{224}Ra group. If it is assumed that C_1 , C_2 , and C_3 are the measured count rates from the integration of the ^{232}U , ^{228}Th and ^{224}Ra peaks

in the uranium spectrum respectively then the corrected count rate C'_1 for ^{232}U peak can be obtained from:

$$C'_1 = C_1 - (0.4085 C_2 - 0.0215 C_3)$$

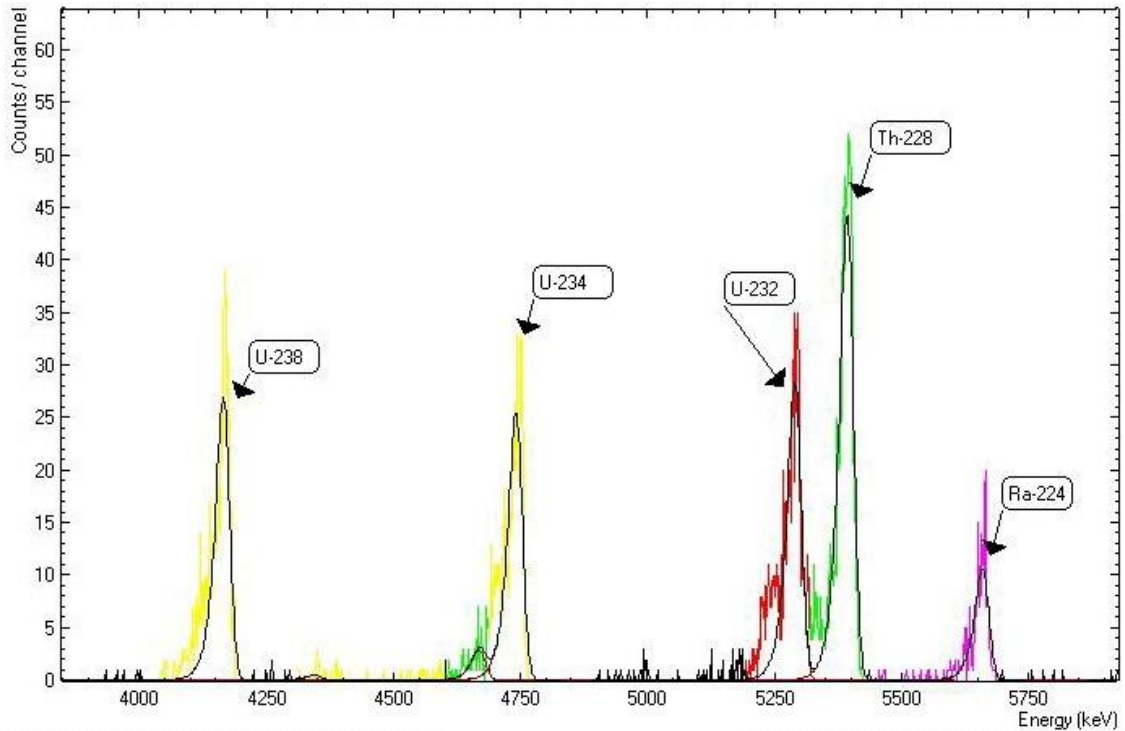


Fig.(3.2): Typical α -particle spectrum of natural uranium

Table (3.1): Half-lives and energies of uranium isotopes

Isotope	Half-life	α -energy (MeV)
^{232}U	72 y	5.32 (68%) – 5.26 (32%)
^{228}Th	1.19 y	5.42 (73%) – 5.34 (27%)
^{224}Ra	3.6 d	5.69 (95%) – 5.44 (5%)
^{238}U	4.51E9 y	4.20 (79%) – 4.15(21%)
^{234}U	2.47E5 y	4.77 (71%) - 4.72 (28%)
^{235}U	7.1E8 y	4.4(57%), 4.37(18%), 4.58(8%)

3.6.5 Calculation of uranium activity concentration in the samples:

Given the corrected count rates for each peak in the sample α -spectrum, the activity (A) of each radionuclide (^{238}U and ^{234}U) in the sample (Bg/kg) was calculated as:

$$A = \frac{\text{Sample counts} * A^{\circ} \text{ (mBq)}}{\text{Tracer counts} * \text{Sample weight (g)}}$$

Where, A° is the initial activity of the added tracer.

3.6.6 Chemical yield estimation:

The chemical yield or extraction recovery of uranium was obtained from the observed ^{232}U tracer counts in their respective spectra. The percentage chemical yield (Y %) is calculated from:

$$Y\% = \frac{A * 100}{A^{\circ}}$$

Where A° is the initial activity of the added tracer and A (Bq) is the fraction of the absolute activity of the tracer actually deposited on the disc and is given by:

$$A = \frac{\text{Tracer counts}}{\text{counting efficiency} * \text{Counting time (sec)}}$$

The average counting efficiency of the used system is 18% as calculated by preparing standard source by direct evaporation of 17.67 mBq of ^{232}U tracer. It was calculated using the following equation:

$$\text{Counting efficiency} = \frac{\text{Tracer counts} * 100}{A * \text{Counting time (sec)}}$$

Where A is the absolute activity of the tracer activity in Bq.

The counting time required to improve the validity of the measurements depends on the activity of the sample, which also governs the amount of tracer to be added (Sam, 1998). On the average, the calculated chemical recovery was 63.3%.

3.7 Elemental analysis using atomic absorption spectrometry:

3.7.1 Sample preparation:

Amounts of ground ore (~ 0.5 g), green solution (1 ml), crude and purified yellow cake (~ 0.5 g) were weighed in suitable beakers. 5 ml of concentrated nitric acid was added to the samples of green solution and heated on a hotplate for 1.5 hour and evaporated to near dryness. 2.5 ml of 8M nitric acid was added and heated till completely dissolved and evaporated to near dryness. The residue was diluted by distilled water and transferred to 50 ml volumetric flask. The beaker was rinsed with 10% nitric acid and completed to the mark.

5 ml concentrated nitric acid and 4 ml 40% HF were added to the ore samples in a Teflon beaker and kept at room temperature for 2 hours for initial reaction and 10 ml of HClO₄ acid was added and heated on a hotplate for 6 hours and evaporated to dryness. 5ml of concentrated nitric acid was added to the residue and heated on a hotplate to near dryness and diluted with distilled water and transferred to 50ml volumetric flask. The beaker rinsed with 10% nitric acid and completed to the mark.

5 ml of concentrated nitric acid was added to the purified yellow cake samples and heated on a hotplate for 2 hours and evaporated to dryness. 2.5 ml HClO₄ was added and heated on a hotplate to near dryness. 2.5 ml 8 M nitric acid was added to dissolve the residue and transferred to 50 ml volumetric flask and the beaker rinsed with 10% nitric acid and completed to the mark.

10 ml HNO₃ was added to the crude yellow cake samples and heated on a hotplate for 2 hours and evaporated to near dryness. 5 ml of 8M HNO₃ was added to the residue and heated till dissolved and evaporated to near dryness. The residue was dissolved in 2M HNO₃ and transferred to 50 ml volumetric flask and the beaker rinsed with 2M HNO₃ and completed to the mark.

1.00 ml of concentrated sulfuric acid was placed in two different beakers and 10 ml of concentrated HNO₃ was added and heated on a hotplate for 2 hours and evaporated to near dryness. 5 ml of 8M HNO₃ was added to the residue and evaporated to near dryness and the residue dissolved in 2M HNO₃ and transferred to 50 ml volumetric flask and the beaker rinsed with 2M HNO₃ and completed to the mark.

3.7.2 Preparation of stock standard solutions:

Stock standard solutions containing 1000 ppm of copper, zinc, cadmium, calcium, manganese, iron, nickel, and lead were obtained from Prim Ag[®] -Plus Certified reference material. Specifications of these stock solutions are shown in Table 3.2.

Table (3.2): Specification of stock standard solutions

Element	Solute	Matrix
Ca	CaCO ₃	HNO ₃ (0.5M)
Mn	Mn (Metal)	HNO ₃ (0.5M)
Fe	Fe(NO ₃) ₃ .9H ₂ O	HNO ₃ (0.5M)
Cu	Cu (Metal)	HNO ₃ (0.5M)
Zn	Zn (Metal)	HNO ₃ (0.5M)
Cd	Cd (Metal)	HNO ₃ (0.5M)
Pb	Pb (metal)	HNO ₃ (0.5M)
Ni	Ni (Metal)	HNO ₃ (0.5M)

3.7.3 AAS working conditions:

Perkin Elmer AAS model 2380 was used for the measurement of elemental concentrations namely, Ca, Mn, Fe, Cu, Zn, Cd, Ni, and Pb in the samples under the following settings of wavelength and lamp current (Table 3.3).

Table (3.3): The settings of wavelength, lamp current and slit-width of AAS

Element	Wave length (nm)	Hallow cathode current (mA)	Slit-width (nm)
Fe	248.3	12.00	0.20
Mn	279.5	10.00	0.20
Zn	213.9	08.00	0.50
Ni	232.0	12.00	0.20
Pb	283.3	10.00	1.00
Cd	228.8	08.00	1.00
Cu	324.8	06.00	0.50
Ca	422.7	10.00	0.50

3.7.4 Procedure:

A series of working standard solutions were prepared from the stock solution of each element depending on the sensitivity range specified in the manual of the AAS. About 20 ml of each of the working standard solutions and sample solution were separately placed into 50 ml beaker. After an allowed warming up period for the spectrometer, the blank (zero ppm standards) was set to zero deflection. Sample solutions were aspirated into the flame under the same conditions as the working standard solutions. The calibration curves of absorbance versus concentration as shown in the Appendix (Figs. 3.3-3.10), were plotted using integrated software program with the instrument, and the concentrations of the analyte (ppm) in the sample were determined. International Atomic Energy Agency (IAEA) certified reference material (Soil-7) was used as a quality control sample throughout the measurement period in order to confirm the consistency of the system. Comparison between the measured and the certified values with their relative error which is the measure of accuracy are shown in Table (3.4)

Table (3.4): Comparison between the certified and measured value for some elements by AAS in reference material (soil-7)

Element	Recommended value (ppm)	Measured value (ppm)	Absolute error (%)
Cd	1.3	0.97	25.4
Fe	25700	26250.38	2.14
Ca	163000	161985	0.62
Zn	104	117.22	12.71
Ni	26	22.8	12.31
Cu	11	10.99	0.10
Mn	631	691.48	9.58
Mg	11300	11572.72	2.41
Pb	60	65.42	9.03

CHAPTER FOUR
RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

Table 4.1 presents the average activity concentration of ^{238}U (Bq/kg or Bq/l), its equivalent mass concentration (ppm), and $^{234}\text{U}:$ ^{238}U activity ratio in ore, green solution, crude yellow cakes (before iron separation SDU1, ADU1, $\text{UO}_3 \cdot x\text{H}_2\text{O}$), after iron separation SDU, ADU, $\text{UO}_3 \cdot x\text{H}_2\text{O}$) and purified yellow cake samples. The average mass concentration of uranium in ore was found to be 119.38 ± 79.66 ppm which corresponds to 0.012%. This mass concentration falls within concentration of uranium considered as unconventional resource where uranium recovery is only possible as a by-product of phosphoric acid production or phosphate fertilizer industry (Bouwer et.al.1978). It is well known that the average grade of world's economic uranium deposits ranging from 0.02% (South Africa) to 0.12% (USA). Brinck,(1974). The ($^{234}\text{U}:$ ^{238}U) activity ratio was not much deviated from unity implying that isotopic fractionation during hydrometallurgical process (i.e. dissolution, extraction, precipitation, separation and purification) is unnoticeable.

Table (4.1): Average activity concentration of ^{238}U (Bq/kg or Bq/l), its equivalent mass concentration (eU in ppm), and $^{234}\text{U}:$ ^{238}U activity ratio in ore, green solution, crude yellow cakes before iron separation SDU1, ADU1, $\text{UO}_3 \cdot x\text{H}_2\text{O}$ 1, after iron separation SDU, ADU, $\text{UO}_3 \cdot x\text{H}_2\text{O}$) and purified yellow cake samples

Sample	^{238}U activity	eU (ppm)	$^{234}\text{U}:$ ^{238}U
Phosphate rocks	1468.29±979.78	119.38±79.66	0.82±0.07
Green solution	711.39±251.50	57.85±20.46	0.94±0.04
SDU1	194.23±121.67	15.79±9.89	0.91±0.10
ADU1	329.3±124.79	26.77±10.15	0.91±0.09
$\text{UO}_3 \cdot x\text{H}_2\text{O}$ 1	372.21±18.05	30.26±1.47	1.07±0.01
SDU	60.14±3.30	4.89±0.27	0.94±0.03
ADU	682.95±10.03	55.52±0.82	0.96±0.01
$\text{UO}_3 \cdot x\text{H}_2\text{O}$	70.35±30.56	5.72±2.48	1.04±0.34
Purified yellow-cake	778985.46±2107.8	6421.63±171.31	0.86±0.06

Note: 1.00 μg of ^{238}U = 12.3 Bq

It might be useful to recall that, during this study leaching process was carried out using plastic containers. Taking into account the high heat evolved during reaction of sulphuric acid with powdered rock phosphate, to avoid any possible adverse heat effect, stainless steel vessel is recommended for that purpose. Similarly, in the separation of resulting green phosphoric acid solution from the slurry of ground rock phosphate filtration method using filter paper was found very slow, time consuming and hence being replaced by centrifugation followed by decantation of clear supernatant solution. However, for large-scale extraction process a more efficient system for separating green solution must be thought off.

Moreover, prior to precipitation of uranium from the green liquor, iron was precipitated to avoid its interference with uranium during later solvent extraction step. Iron was precipitated at pH 3.5 with the addition of saturated magnesium oxide, however, it was observed that another precipitate was formed before reaching the optimum pH (3.5), this problem was attributed to solubilization of aluminum silicate presence in the mother rock with the action of concentrated acid and high temperature forming silicic acid as a gelatinous colloid. Presence of fluoride ion in solution will catalyze the polymerization of silica eventually transforming it into a precipitate. This precipitation reaction is expected to be significantly accelerated below pH (1.8) and at reacting temperature exceeding 45⁰C (IAEA, 1993). Cooling and working with dilute pregnant liquor can overcome this problem of colloidal formation by silica. Alternatively, passing the pregnant liquor through activated charcoal will get rid of silicic colloids via adsorption.

The average mass concentration of uranium, some elements (Pb, Cd, Fe, Zn, Mn, Cu) in ore material, resulting green phosphoric acid solution and the respective percentages of dissolution from the powdered rock phosphate ore are given in Table 4.2. The above mentioned elements have selected to follow their concentrations from the ore down to the purified yellow cake because according to the specifications of commercial yellow cake stated in literature their concentration must not exceed certain limits. Our follow-up at different stages of the extraction process will give a clue of their extracting pathway.

As it could be seen in the last column of Table 4.2, the percent of dissolution of uranium from the ore material (mixed sample from Uro and Kurun deposit located in

the eastern part of the Nuba Mountains) into green solution is about 48%. This percent of dissolution is considered to be very low compared to relevant data in international literature. For instance, Weterings and Janssen (1985) indicated that more than 80% of uranium associated with phosphates dissolved upon treatment of ore with sulfuric acid. This low percentage of uranium leaching may be due to the failure of our experimental set-up to maintain low value of pH during the leaching process; as a consequence phosphate ion concentration can lead to reprecipitation of uranium as well as complexing with ferric ions and thus inhibiting its known role in oxidation of uranium. On the other hand, more than 80% of nickel, zinc, manganese, and copper present in the ore have been taken into solution, while it was poor for Pb (20%), Cd (34%) and Fe (18%).

Table (4.2): Mean concentration (ppm) of uranium and some elements (Pb, Cd, Fe, Zn, Mn, Cu) in ore material, resulting green phosphoric acid solution and the respective percentages of dissolution from the ore

Element	Ore (ppm)	Green solution (ppm)	Percent dissolution (%)
²³⁸ U	119.38±79.66	57.85±20.46	48.46
Pb	14.78±3.89	2.92±.03	19.76
Ni	50.07±1.65	54.81±7.25	109.46
Cd	14.97±0.42	5.15±.716	34.57
Fe	6164.45±592.63	1082.17±89.88	17.56
Zn	2128.24±307.03	2077.71±79.85	97.63
Mn	345.8±12.70	285.55±25.47	82.57
Cu	755.77±14.46	750.12±80.71	99.25

As stated earlier iron in the green solution was separated by precipitation with saturated MgO solution at pH 3.5 and filtered off and the filtrate was tested for the presence of Fe by adding one drop of 2,2'-bipyridine (10 mg/ml in ethanol), and SCN⁻ separately to small amount of the filtrate in a test tube. Colorless of the filtrate with both reagents (bipyridine and SCN⁻) indicates the absence of Fe, however, after analysis of different crude yellow cakes precipitated in the form of ammonium diuranate (ADU), sodium diuranate (SDU) and hydrated uranium trioxide (UO₃.xH₂O) the iron was found but its

concentration was less in contrast to crude yellow cakes precipitated before iron separation.

Tables (4.3) and (4.4) present comparison of iron content in different crude yellow cakes, precipitated before and after iron separation. Iron separation experiment was repeated and it has been confirmed that iron was present in produced crude yellow cakes as shown in Fig. (4.1). It seems that iron test method with 2,2'-bipyridine (10 mg/ml in ethanol), and SCN^- gives false positive result. This could be attributed to the presence of more stronger iron complexing agents in green solution possibly phosphate ion which might form complexes with iron and made it unavailable to react with testing agents (2,2'-bipyridine and SCN^-).

The failure to remove iron completely from green solution by magnesium oxide precipitation method may be due to experimental conditions used in term of pH (3.5), reaction temperature and reaction time not optimal since the precipitation reaction is pH and temperature dependent. Of course, the iron remaining in crude yellow cake will pose serious problems in later purification stage as it follows uranium during extraction (Stas et al., 2002; El-Nadi and Daoud, 2004). Moreover, iron remaining in the extract precipitates as hydroxide and hence during subsequent carbonate stripping can scavenge uranium (Singh et al., 2006). Therefore, it would be necessary for further studies to give much attention on maintaining favorable conditions (pH, temperature and timing) to separate iron prior to precipitation of uranium in order to avoid such inherent co-extraction problem.

It has been well documented that amongst precipitants used for precipitation of uranium, magnesium oxide was found to give relatively the most pure crude yellow cake. Therefore, we have used the ratio of impurity in (ammonium diuranate: hydrated uranium trioxide) and (sodium diuranate: hydrated uranium trioxide) as an index to judge the relative purity level of ammonium diuranate and sodium diuranate. Figure (4.2) and (4.3) illustrated this and it is clear that the levels of impurity in ammonium diuranate is less than sodium diuranate as it indicated by higher impurity ratios.

Table (4.3): Comparison of concentrations (ppm) of uranium and some impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in crude (ADU, UO₃.xH₂O, and SDU) precipitated before iron separation and ratio of impurities relative to UO₃.xH₂O

element	ADU (1)	UO ₃ .xH ₂ O (1)	SDU (1)	Ratio of impurities	
				ADU: UO ₃ .xH ₂ O	SDU: UO ₃ .xH ₂ O
²³⁸ U	26.77±10.15	30.26±1.47	15.79±9.89		
Fe	3457.15±48.36	3066.95±67.79	4435.33±180.37	1.13	1.45
Zn	1703.73±11.32	1452.63±46.5	2136.93±74.88	1.17	1.47
Mn	122.11±1.19	182.50±3.65	168.62±2.48	0.67	0.92
Cu	246.43±7.05	317.17±5.58	971.22±41.67	0.78	3.06
Ni	20.16±0.33	86.38±3.17	27.11±1.22	0.23	0.31
Cd	2.74±0.07	2.12±0.23	3.68±0.02	1.29	1.74
Pb	ND	ND	ND	-	-

Note: LOD of Pb = 0.00013 ppm

Table (4.4): Comparison of concentrations (ppm) of uranium and some impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in crude (ADU, UO₃.xH₂O, and SDU) precipitated after iron separation and ratio of impurities relative to UO₃.xH₂O

element	ADU	UO ₃ .xH ₂ O	SDU	Ratio of impurities	
				ADU: UO ₃ .xH ₂ O	SDU: UO ₃ .xH ₂ O
²³⁸ U	55.52±0.82	5.72±2.48	4.89±0.27		
Fe	2035.13±641.09	208.66±5.39	277.89±5.11	9.75	1.33
Zn	4789.44±169.19	1471.11±53.27	17616.41±491.17	3.26	11.97
Mn	387.91±2.35	212.45±1.84	4691.84±536.03	1.83	22.08
Cu	1434.78±489.20	305.06±6.18	2562.27±29.62	4.70	8.40
Ni	191.89±8.02	82.65±1.39	781.52±51.15	2.32	9.46
Cd	7.73±0.41	2.12±0.23	24.17±0.05	3.65	11.40
Pb	ND	ND	10.68±3.41	-	-

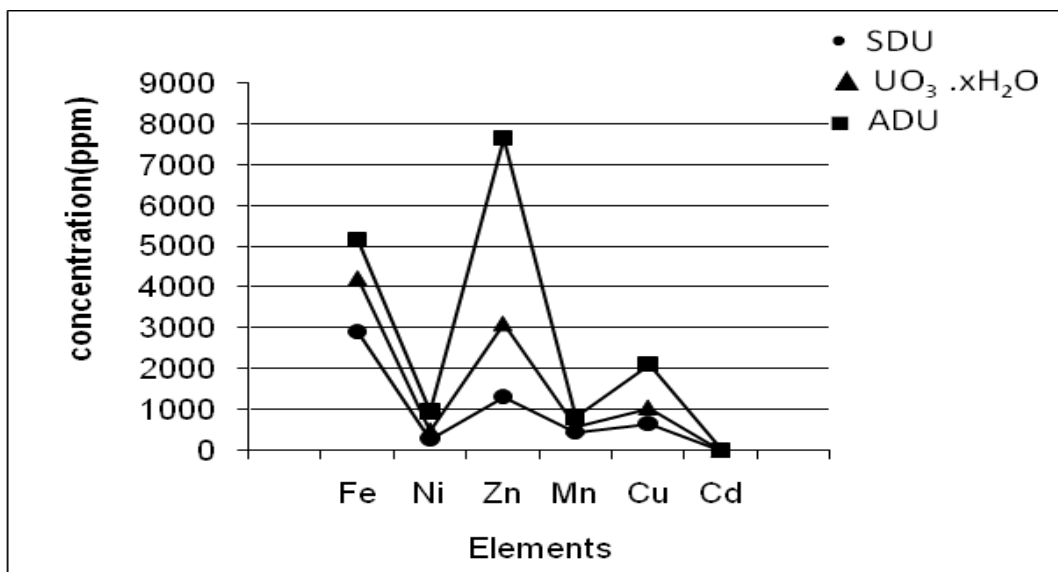


Fig. (4.1): Plot showing comparison of concentration (ppm) of some impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in crude sodium diuranate, ammonium diuranate and hydrated uranium trioxide which precipitated after iron separation

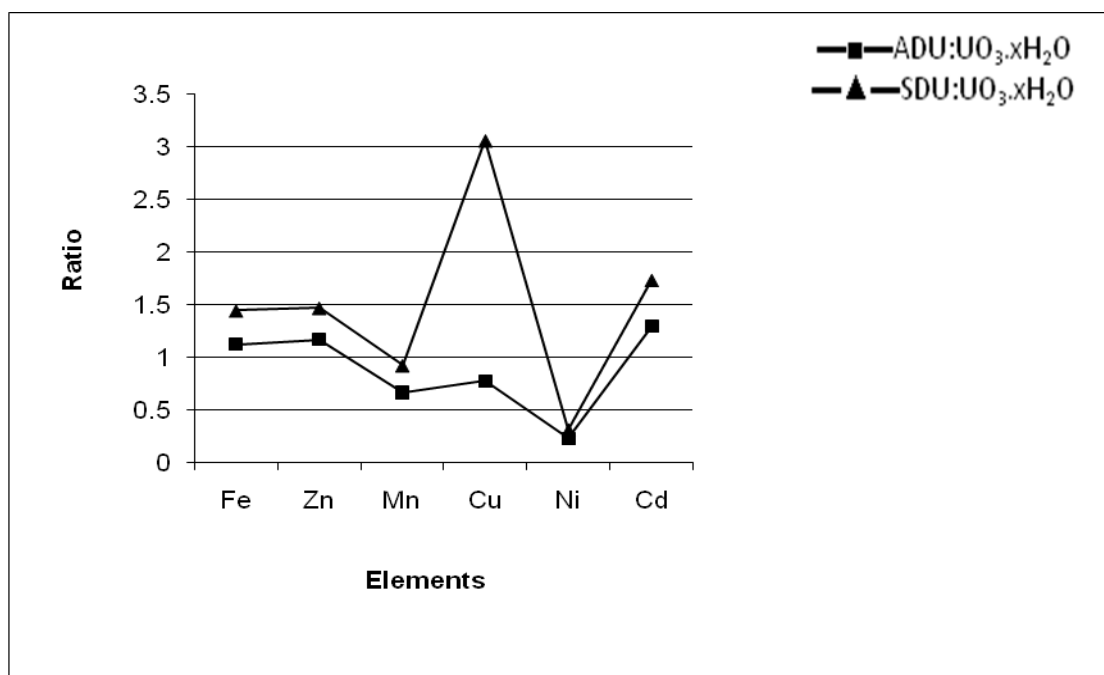


Fig. (4.2): Plot shown ratio of impurities in (ammonium diuranate: hydrated uranium trioxide) and (sodium diuranate: hydrated uranium trioxide) precipitated before iron separation

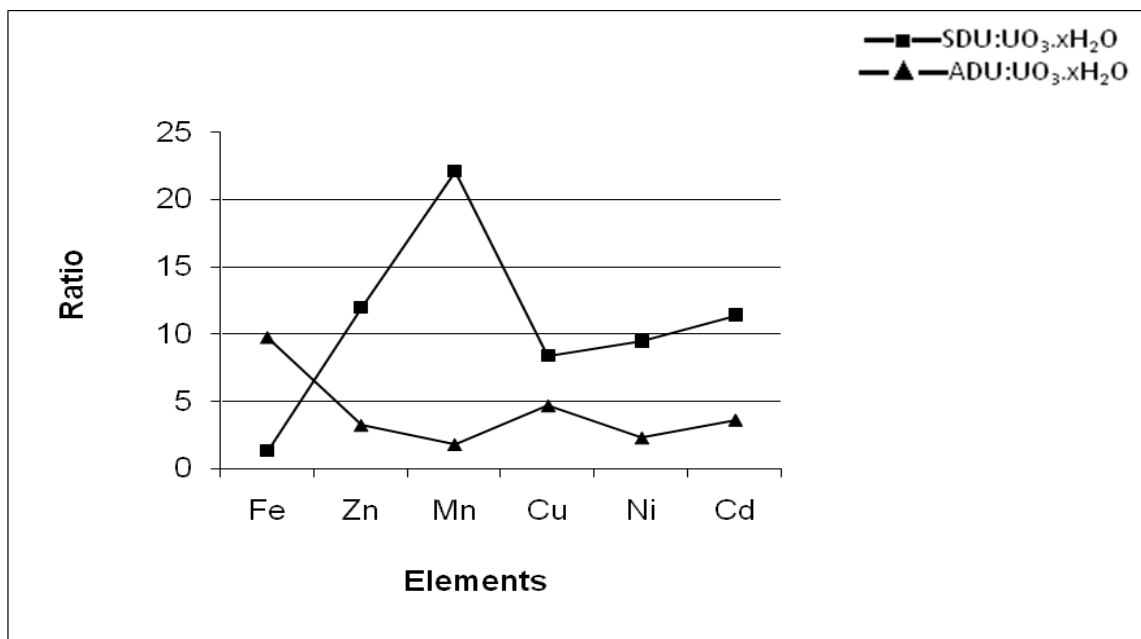


Fig.(4.3): Plot shown ratio of impurities in (ammonium diuranate: hydrated uranium trioxide) and (sodium diuranate: hydrated uranium trioxide) precipitated after iron separation.

The effect of iron separation on uranium concentration and other impurities in the three forms of yellow cakes is separately presented below. In ammonium diuranate (ADU) as shown in Table (4.5) the amount of uranium precipitated after iron separation was twice more than the quantity of it in one precipitate before iron separation. This has been revealed from (ADU:ADU1) ratio. Also concentration of other impurities such as Ni, Cd, Mn, Cu and Zn was increased by a factor of 9.5, 2.82, 3.18, 5.82 and 2.81, respectively, compared with (ADU) precipitated before iron separation. This increase is apparently illustrated by (ADU:ADU1) factor and Fig. (4.4) which show similar trends with different concentrations.

Table (4.5): Comparison of concentrations (ppm) of uranium and some impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in crude ammonium diuranate precipitated before iron separation (ADU1) and after iron separation (ADU) and ADU: ADU(1) ratio

element	ADU (1)	ADU	ADU : ADU(1)
²³⁸ U	26.77±10.15	55.52±0.82	2.07
Fe	3457.15±48.36	2035.13±641.09	0.59
Zn	1703.73±11.32	4789.44±169.19	2.81
Mn	122.11±1.19	387.91±2.35	3.18
Cu	246.43±7.05	1434.78±489.20	5.82
Ni	20.16±0.33	191.89±8.02	9.52
Cd	2.74±0.07	7.73±0.41	2.82
Pb	ND	ND	-

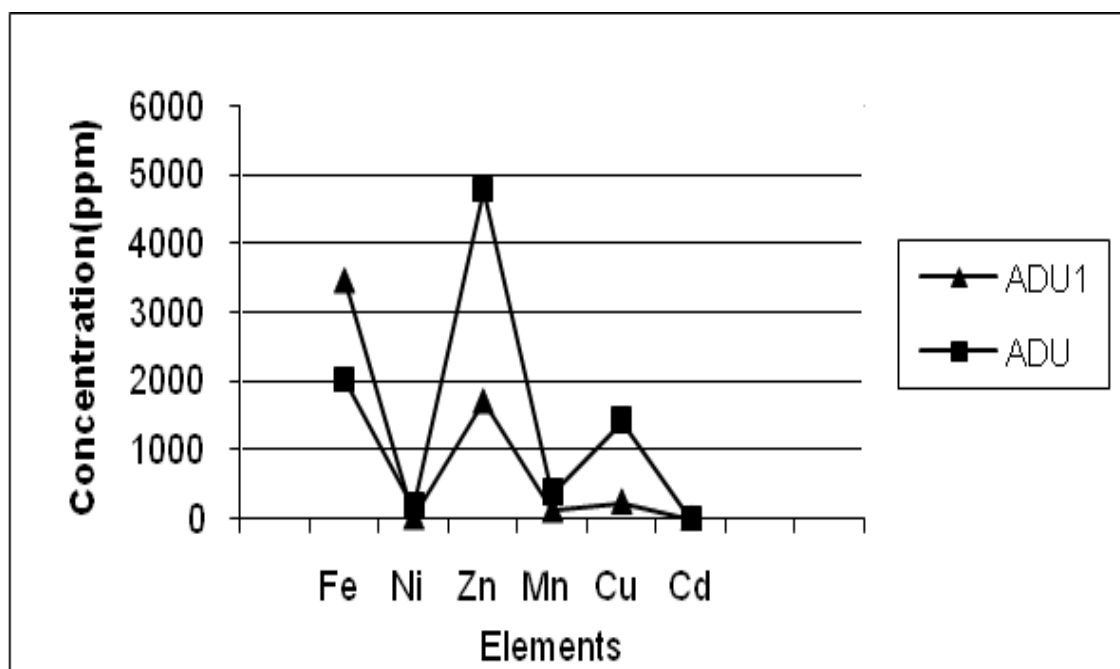


Fig. (4.4): Plot showing comparison of concentration (ppm) of some impurities (Fe, Zn, Mn, Cu, Ni and Cd) in crude ammonium diuranate precipitated before iron separation (ADU1) and after iron separation (ADU)

Similarly, uranium content in crude ($\text{UO}_3 \cdot x\text{H}_2\text{O}$) precipitated before iron separation is five times more than that in $\text{UO}_3 \cdot x\text{H}_2\text{O}$ precipitated after iron separation as depicted in Table 4.6. There seems very slight difference in the content of Ni, Cd, and Cu, Zn and Mn in crude $\text{UO}_3 \cdot x\text{H}_2\text{O}$ precipitated before and after iron separation as could be deduced from the ratio of impurities between ($\text{UO}_3 \cdot x\text{H}_2\text{O}:\text{UO}_3 \cdot x\text{H}_2\text{O}(1)$) and semi-identical pattern shown in Fig.(4.5).

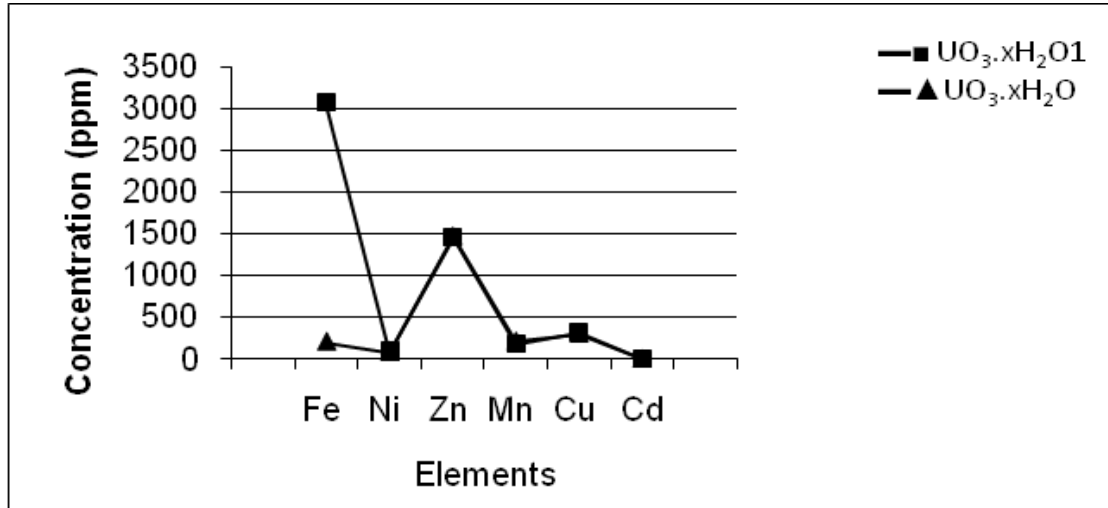


Fig. (4.5): Plot showing the concentrations (ppm) of some impurities (Fe, Zn, Mn, Cu, Ni and Cd) in crude hydrated uranium trioxide precipitated before iron separation ($\text{UO}_3 \cdot x\text{H}_2\text{O}(1)$) and after iron separation ($\text{UO}_3 \cdot x\text{H}_2\text{O}$)

Table (4.6): Comparison of concentrations (ppm) of uranium and some impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in crude $\text{UO}_3 \cdot x\text{H}_2\text{O}$ precipitated before and after iron separation and their respective ratios

element	$\text{UO}_3 \cdot x\text{H}_2\text{O} (1)$	$\text{UO}_3 \cdot x\text{H}_2\text{O}$	$\text{UO}_3 \cdot x\text{H}_2\text{O} : \text{UO}_3 \cdot x\text{H}_2\text{O}(1)$
^{238}U	30.26 ± 1.47	5.72 ± 2.48	0.19
Fe	3066.95 ± 67.79	208.66 ± 5.39	0.07
Zn	1452.63 ± 46.5	1471.11 ± 53.27	1.01
Mn	182.50 ± 3.65	212.45 ± 1.84	1.16
Cu	317.17 ± 5.58	305.06 ± 6.18	0.96
Ni	86.38 ± 3.17	82.65 ± 1.39	0.96
Cd	2.12 ± 0.23	1.71 ± 0.04	0.80
Pb	ND	ND	-

As shown in Table 4.7 for crude sodium diuranate (SDU) precipitated before iron separation its uranium content is three-fold than that in crude sodium diuranate (SDU) precipitated after iron separation. Also it seems that Zn, Mn, Cu, Cd, and Ni content in crude sodium diuranate (SDU) precipitated after iron separation is more by a factor of 8.24, 27.83, 2.64, 6.56, and 28.83, respectively, in contrast to (SDU) precipitated before iron separation as it has been demonstrated by their respective ratios in SDU: SDU1 (Fig. 4.6).

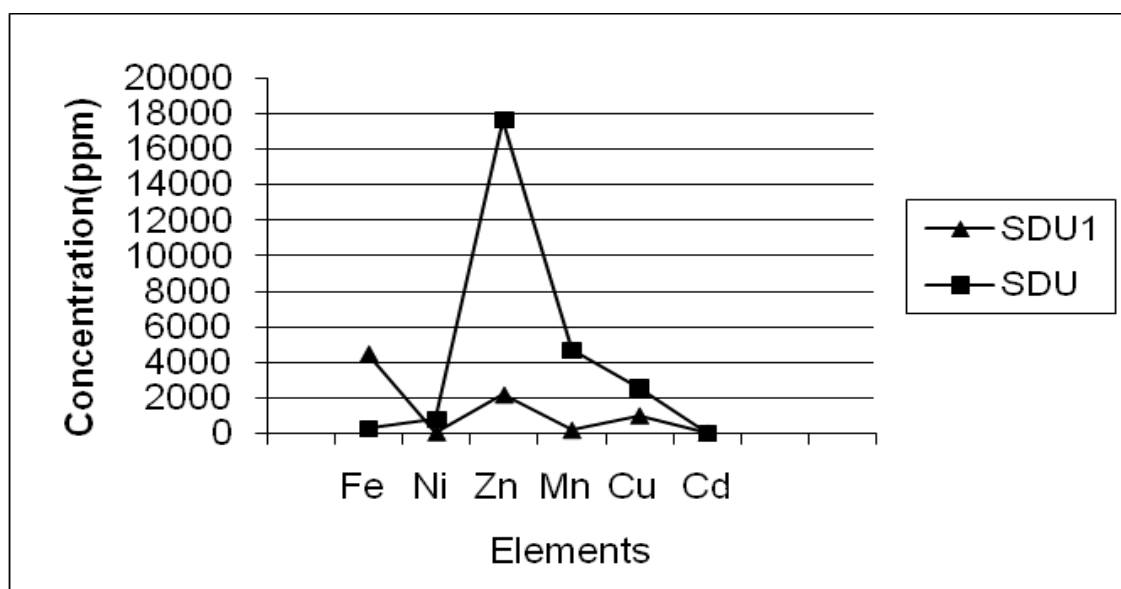


Fig.(4.6): Plot showing comparison of concentration (ppm) of some impurities(Fe, Zn, Mn, Cu, Ni and Cd) in crude sodium diuranate precipitated before iron separation(SDU1) and after iron separation (SDU)

Table (4.7): Comparison of concentrations (ppm) of uranium and some impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in crude sodium diuranate precipitated before iron separation (SDU1) after iron separation (SDU) and their respective ratios

element	SDU (1)	SDU	SDU1:SDU
²³⁸ U	15.79±9.89	4.89±0.27	0.31
Fe	4435.33±180.37	277.89±5.11	0.06
Zn	2136.93±74.88	17616.41±491.17	8.24
Mn	168.62±2.48	4691.84±536.03	27.83
Cu	971.22±41.67	2562.27±29.62	2.64
Ni	27.11±1.22	781.52±51.15	28.83
Cd	3.68±0.02	24.17±0.05	6.56
Pb	ND	10.68±3.41	-

Upon comparing the mass concentration of uranium in the three forms of crude yellow cakes which were precipitated from the green solution it follows the order: $\text{UO}_3 \cdot x\text{H}_2\text{O} >$ ammonium diuranate $>$ sodium diuranate (Table 4.3). However, this order of mass concentration of uranium in crude yellow cakes was changed after iron separation, it was as follows: ADU $>$ $\text{UO}_3 \cdot x\text{H}_2\text{O} >$ SDU (Table 4.4). If this order is combined with the concentration of impurities, it is obvious that the higher the pH of the precipitation medium the more impure product would be produced, this is clear from the impurity ratios in (ADU: $\text{UO}_3 \cdot x\text{H}_2\text{O}$) and (SDU: $\text{UO}_3 \cdot x\text{H}_2\text{O}$) as presented Table (4.3) and (4.4); and in Fig (4.2) and Fig (4.3).

With regard to which precipitant gives relatively pure precipitation, it could be said that saturated magnesia and ammonia are seemed less aggressive which agrees with literature findings, compared to sodium hydroxide as reflected by the level of impurities encountered.

The level of impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in the purified yellow cake is less than that set for commercial products with the exception of Cd as shown Table 4.8.

Table (4.8): Comparison of percentage of impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in purified yellow-cake produced with that specified in the standard commercial product

Element	Standard yellow-cake (%)	Yellow-cake produced (%)
V	0.13	ND
Pb	0.70	0.01
Ni	-	0.03
Zr	0.5	ND
Cd	~ 0.0	0.01
Fe	1.00	0.15
Cr	0.01	ND
Zn	-	0.07
Mn	-	0.01
Mo	0.15	ND
Th	2.00	ND
Cu	0.03	0.02

CONCLUSION

Based on the results obtained in this study it could be concluded that:

1. The average mass concentration of uranium from Uro and Kurun rock phosphate falls within concentration of uranium considered as unconventional resource where uranium recovery is only possible as a by-product of phosphoric acid production or phosphate fertilizer industry.
2. There is no noticeable isotopic fractionation observed during hydrometallurgical process since the ratio of uranium isotopes $^{234}\text{U}:$ ^{238}U at different stages of the process (i.e. dissolution, extraction, precipitation, separation and purification) not much deviating from unity.
3. The percent of uranium dissolution from Uro and Kurun rock phosphate is very low (48%) indicating that careful maintaining of experimental set-up with respect to dissolution temperature, pH, quality of sulphuric acid and its optimum concentration, and reaction time might solve this problem of low solubility.
4. Iron test method with 2,2'-bipyridine (10 mg/ml in ethanol), and SCN^- gives false positive results, this could be attributed to the presence of more stronger iron complexing agents in green solution possibly phosphate ion.
5. Iron was not removed completely by MgO precipitation under experimental conditions (pH 3.5, temperature and retention time) used in this study. However, different forms of crude yellow cakes precipitated after iron separation contain high concentrations of impurities in contrast to those precipitated before iron separation
6. Saturated magnesia and ammonia are seemed less aggressive precipitants for uranium from sulphuric acid leachate compared to sodium hydroxide as reflected by the level of impurities encountered.
7. TBP proved to be an efficient solvent for purification of uranium from nitrate media since the level of impurities encountered matching those specified for commercial yellow cake.

RECOMMENDATION

To overcome the problems encountered during this study, we recommend the following:

1. Further studies should use stainless steel containers in leaching process and consider more efficient filtration or centrifugation method to separate the leachate to avoid long retention time of slurry.
2. Further studies should keep stringent experimental set-up in term of pH value for precipitation of iron from the green phosphoric acid prior to precipitation of uranium in order to avoid co-extraction problem.

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APPENDIX

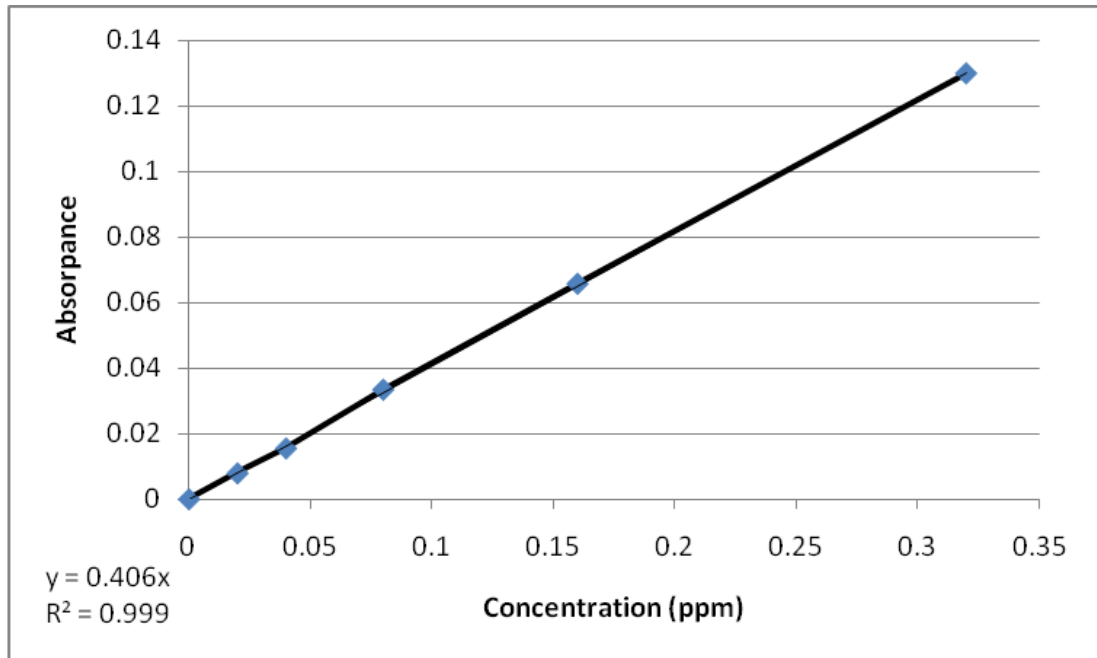


Fig. (3.3): Calibration curve of AAS for Cd

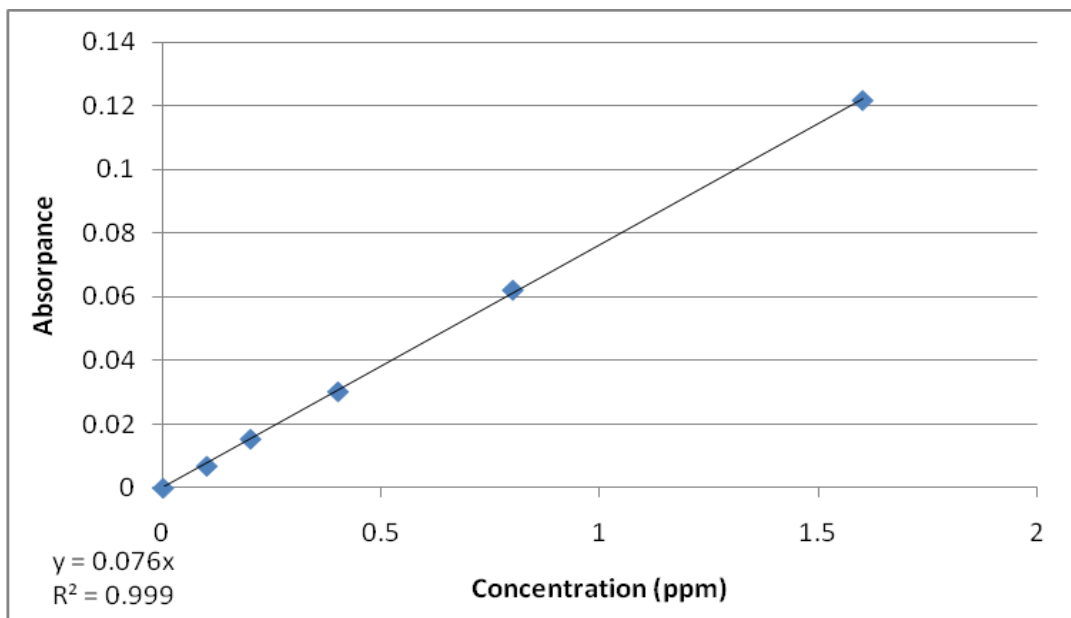


Fig. (3.4): Calibration curve of AAS of Ni

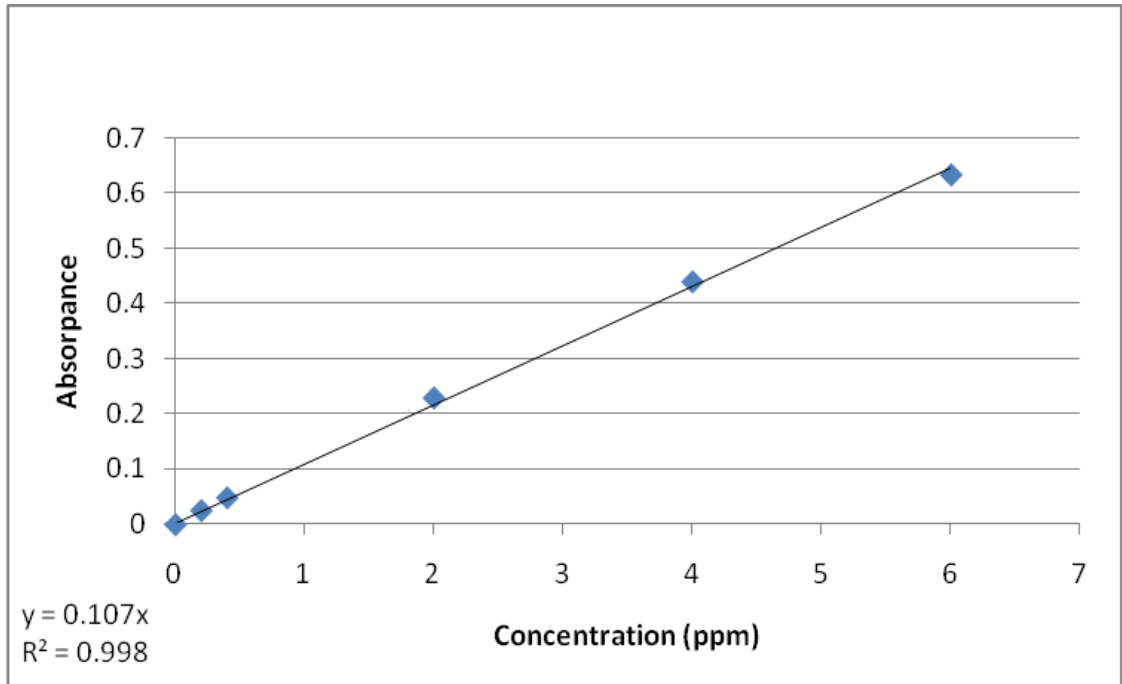


Fig. (3.5): Calibration curve of AAS for Cu

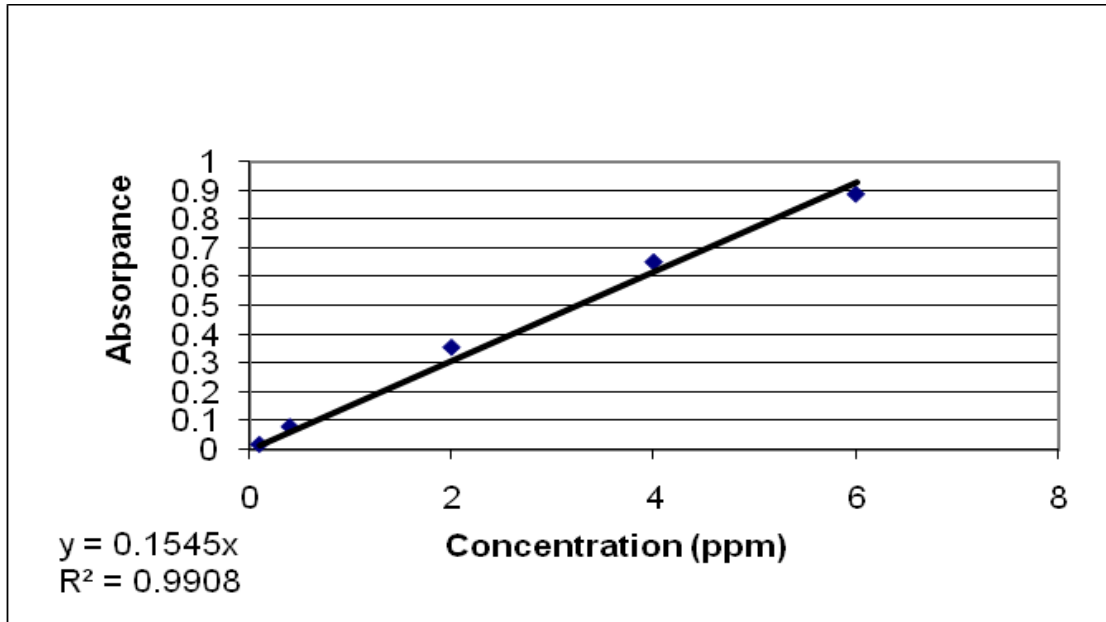


Fig. (5.6): Calibration curve of AAS for Mn

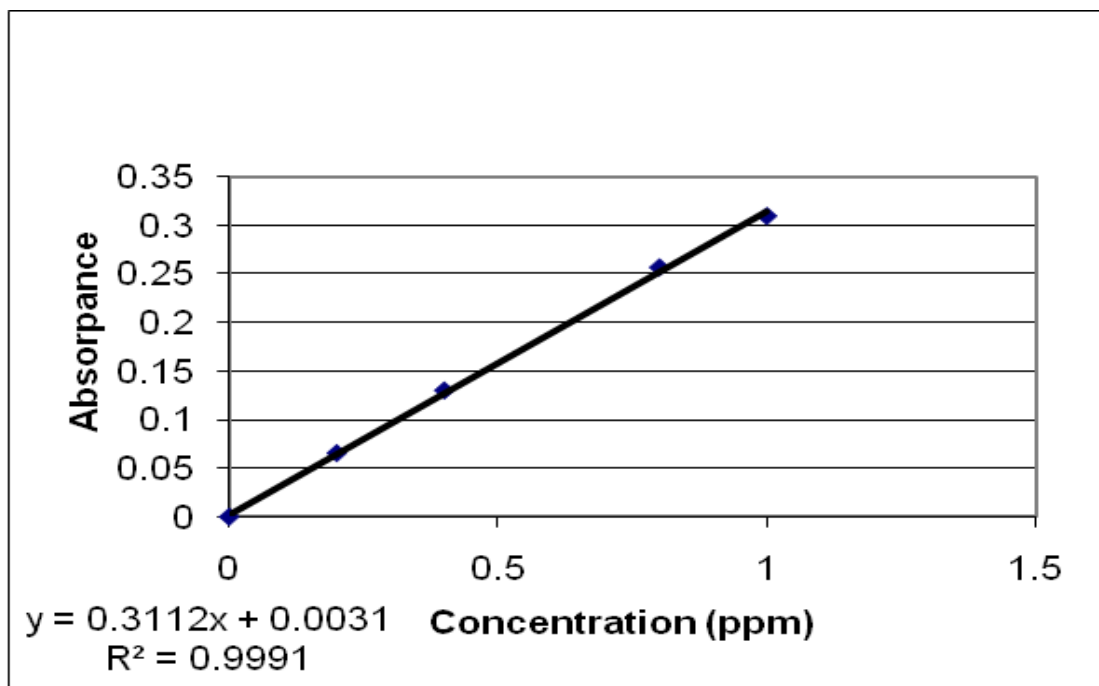


Fig. (3.7): Calibration curve of AAS for Zn

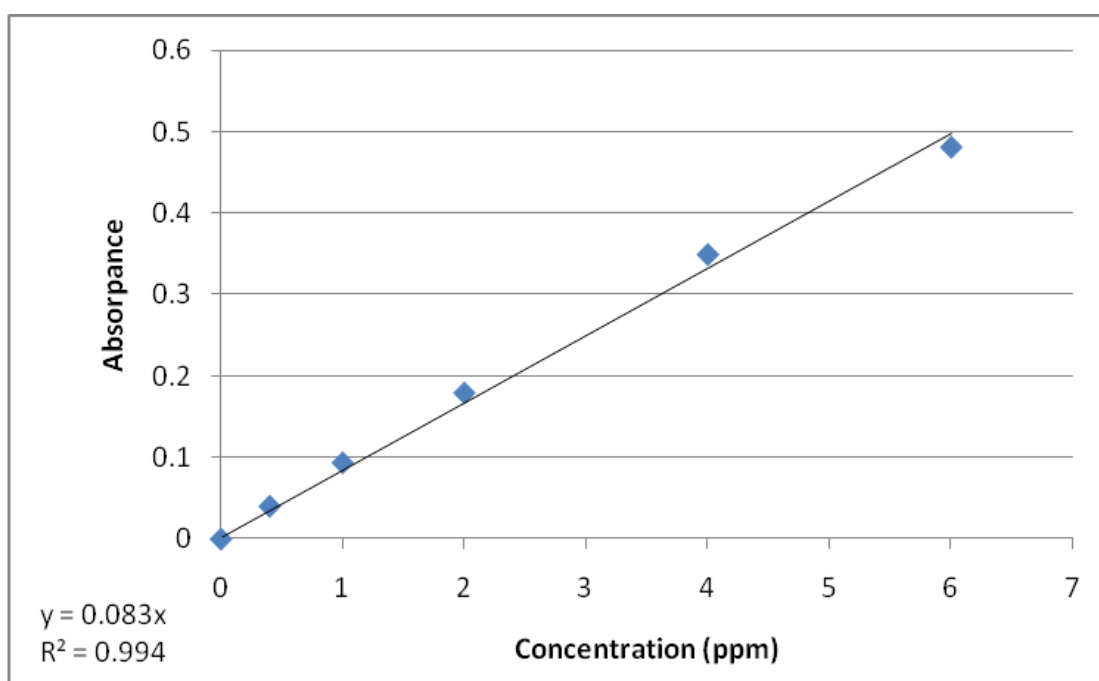


Fig. (3.8): Calibration curve of AAS for Fe

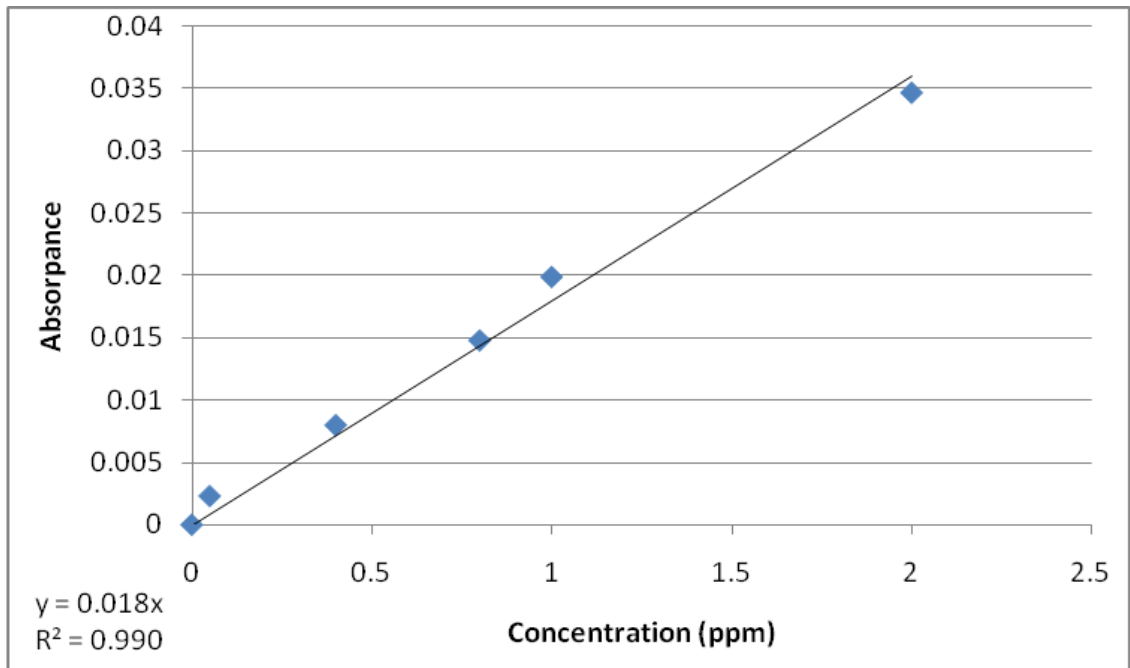


Fig. (3.9): Calibration curve of AAS for Pb

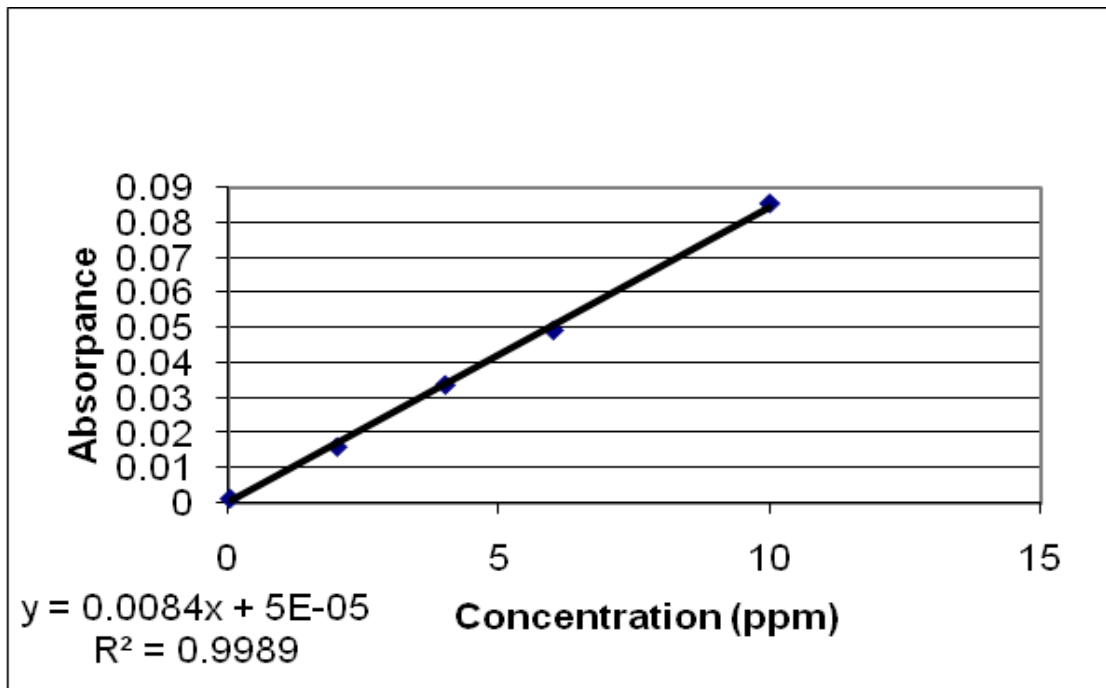


Fig. (3.10): Calibration curve of AAS for Ca