

## Precipitation and purification of uranium from rock phosphate

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### ABSTRACT

This study was carried-out to leach uranium from rock phosphate using sulphuric acid in the presence 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  $(Na_2 U_2 O_7)$  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, atomic absorption spectroscopy (AAS) was used for determination of impurities (Pb, Ni, Cd, Fe, Zn, Mn, and Cu). On the average, the equivalent mass concentration of uranium was  $119.38 \pm 79.66$  ppm (rock phosphate) and  $57.85 \pm 20.46$  ppm (green solution) with corresponding low percent of dissolution (48%) which is considered low. The isotopic ratio ( $^{234}U: ^{238}U$ ) in all stages of hydrometallurgical process was not much differ from unity indicating lack of fractionation. Upon comparing the levels of impurities in different form of crude yellow cakes, it was found that the lowest levels were measured in  $UO_3 \cdot xH_2O$ . 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 forms 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.

### Introduction:

Uranium is known to be genetically related to phosphates to a greater extend, hence it occurs in all types of phosphate rocks with varying concentrations [1]. In sulphuric acid leaching process more than 80% of the uranium originally present in the parent rock phosphate ends up in solution, so that the resulting green phosphoric acid constitute a secondary source for

uranium[2,3]. Recovery of uranium from phosphoric acid is based on solvent extraction methods and precipitation as yellow cakes [4, 5, 6, 7, 8, 9, 10]. A number of precipitants among which sodium hydroxide, ammonium hydroxide, and hydrogen peroxide have proved effective over a wide pH range [11, 12]. In this study, ammonia, magnesium oxide and sodium hydroxide were used as precipitants for precipitation of uranium from green phosphoric acid solution to examine their merits and demerits with respect to accompanying impurities.

## **Material and Methods**

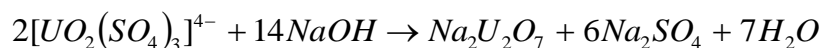
### ***Sample collection, preparation and uranium leaching***

Rock phosphate samples were collected from Uro and Kurun rock phosphate deposits located in eastern part of the Nuba Mountains, Southern Kurdufan State. Details of geological information and scintillometer maps are found elsewhere [13]. The samples were crushed and ground to a suitable size for leaching.

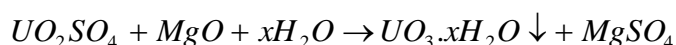
Uranium in the ground ore was leached with 98% H<sub>2</sub>SO<sub>4</sub> in plastic containers commercially used for purchasing sulphuric acid. Potassium chlorate was added as an oxidant. The resulting pregnant liquor (green solution of phosphoric acid) was separated by decantation flowed by centrifugation after diluting with deionized water. Suspended insoluble colloidal material was removed by passing the filtrate through a column packed with activated charcoal.

### ***Precipitation of uranium in different forms of crude yellow-cake***

Sodium diuranate (SDU) was precipitated from the green solution at pH 12 by addition of 30% NaOH. The precipitate was left over-night to settle and then separated by decantation flowed by centrifugation. It was washed with deionized water and dried in an oven at 105°C.

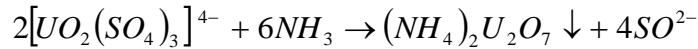


Uranium as hydrated trioxide (UO<sub>3</sub>.xH<sub>2</sub>O) was precipitated with saturated magnesium oxide as a precipitant at pH 7.5. The precipitate was kept over-night and then separated by decantation flowed by centrifugation; washed with deionized water and dried in an oven at 105°C.



The pregnant liquor was heated to 70 °C on a hot plate and uranium was precipitated as crude ammonium diuranate (NH<sub>4</sub>)<sub>2</sub>U<sub>2</sub>O<sub>7</sub> at pH ≈ 7.5 by drop-wise addition of 10% ammonium

hydroxide. The ammonium diuranate was separated by decantation and centrifugation, washed several times with deionized water and dried in an oven at 105°C.



***Purification of crude yellow-cake:***

The crude yellow-cake was purified by extraction with 5% tributyl phosphate (TBP) in kerosene and the uranium was stripped from the organic phase with 0.5 M Na<sub>2</sub>CO<sub>3</sub>, re-precipitated as ammonium diuranate (NH<sub>4</sub>)<sub>2</sub>U<sub>2</sub>O<sub>7</sub> and calcined to UO<sub>3</sub> in furnace at 450°C.

***Measurement of uranium concentration and the associated impurities:***

Uranium concentration in ore, green solution, yellow cake samples was measured using alpha-particle spectroscopy after nitric acid dissolution, TBP extraction, electrodeposition on stainless steel discs. <sup>232</sup>U tracer was used as a yield determinant and the calculated extraction recovery fall within the range of 46.3- 88.4%.

The associated elemental impurities were measured using AAS. IAEA certified reference material (Soil-7) was used as a quality control sample to check the accuracy of the measurement system and the level of relative error for each element was found acceptable.

***RESULTS AND DISCUSSION***

Table 1.1 presents the average activity concentration of <sup>238</sup>U (Bq/kg or Bq/l), its equivalent mass concentration (ppm), and <sup>234</sup>U:<sup>238</sup>U activity ratio in ore, green solution, crude yellow cakes (Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>, (NH<sub>4</sub>)<sub>2</sub>U<sub>2</sub>O<sub>7</sub>, UO<sub>3</sub>.xH<sub>2</sub>O) and purified yellow cake samples. The activity concentration of <sup>238</sup>U in ore samples was highly scattered with an average value of 1468.29 ±979.78 Bq/kg, which corresponds to an equivalent mass of 119.38±79.66 ppm (0.012%). The concentration obtained here is a characteristic of unconventional resources where uranium recovery is only possible as a by- product of phosphoric acid production or phosphate fertilizer industry [14]. It is well known that the average grade of world's economic uranium deposits ranging from 0.02% (South Africa) to 0.12% (USA) [15].The (<sup>234</sup>U:<sup>238</sup>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 (1.1): Average activity concentration of  $^{238}\text{U}$  (Bq/kg or Bq/l), its equivalent mass (eU) (ppm), and  $^{234}\text{U}$ : $^{238}\text{U}$  activity ratio in ore, green solution, crude yellow cakes and purified yellow cake ( $\text{UO}_3$ ) samples**

Sample	$^{238}\text{U}$ activity	eU (ppm)	$^{234}\text{U}$ : $^{238}\text{U}$
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
$\text{Na}_2\text{U}_2\text{O}_7$	194.23±121.67	15.79±9.89	0.91±0.10
$(\text{NH}_4)_2\text{U}_2\text{O}_7$	329.3±124.79	26.77±10.15	0.91±0.09
$\text{UO}_3 \cdot x\text{H}_2\text{O}$	372.21±18.05	30.26±1.47	1.07±0.01
Purified yellow-cake ( $\text{UO}_3$ )	778985.46±2107.8	6421.63±171.31	0.86±0.06

**Note:** 1.00  $\mu\text{g}$  of  $^{238}\text{U}$  = 12.3 mBq

The average concentration of impurities (Pb, Cd, Fe, Zn, Mn, Cu) in ore material, resulting green phosphoric acid solution and their respective percentages of dissolution from the powdered rock phosphate ore are given in Table 1.2. These elements have been selected to follow their concentrations in all stages 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 [11]. The 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 1.2, the percent of dissolution of uranium from the ore material with sulfuric acid 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 [2] 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 complexing of phosphate ions in leachate 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%).

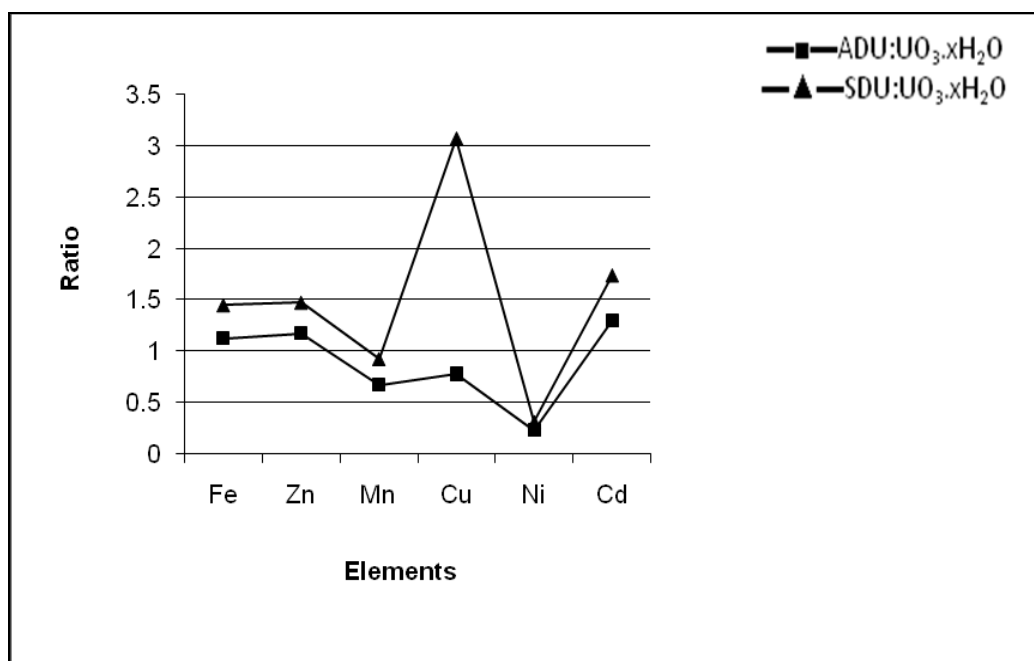
**Table (1.2): Mean concentration (ppm) of uranium and impurities (Pb, Cd, Fe, Zn, Mn, Cu) in ore material, resulting green phosphoric acid solution and the respective percentages of dissolution from the ore**

Element	Ore (ppm)	Green solution (ppm)	(%) dissolution
<sup>238</sup> 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

It has been well documented that amongst precipitants used for precipitation of uranium, magnesium oxide was found to give relatively pure crude yellow cake ( $UO_3 \cdot xH_2O$ ). Therefore, the ratio of impurity in (ammonium diuranate: hydrated uranium trioxide) and (sodium diuranate: hydrated uranium trioxide) was used as an index to judge the relative purity level of ammonium diuranate and sodium diuranate [Table 1.3]. Figure (1.1) illustrates this and it is clear that the level of impurities in ammonium diuranate is less than sodium diuranate as evident from the higher impurity ratios.

**Table (1.3): Comparison of concentrations (ppm) of uranium and impurities (Fe, Zn, Mn, Cu, Ni, Cd and Pb) in crude  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ ,  $\text{UO}_3 \cdot x\text{H}_2\text{O}$ , and  $\text{Na}_2\text{U}_2\text{O}_7$  and ratio of impurities relative to  $\text{UO}_3 \cdot x\text{H}_2\text{O}$**

element	$(\text{NH}_4)_2\text{U}_2\text{O}_7$	$\text{UO}_3 \cdot x\text{H}_2\text{O}$	$\text{Na}_2\text{U}_2\text{O}_7$	Ratio of impurities	
				$(\text{NH}_4)_2\text{U}_2\text{O}_7 : \text{UO}_3 \cdot x\text{H}_2\text{O}$	$\text{Na}_2\text{U}_2\text{O}_7 : \text{UO}_3 \cdot x\text{H}_2\text{O}$
$^{238}\text{U}$	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	-	-



**Fig. (1.1): Plot of ratio of impurities in (ammonium diuranate: hydrated uranium trioxide) and (sodium diuranate: hydrated uranium trioxide)**

Upon comparing the mass concentration of uranium in the three forms of crude yellow cakes it was found in the following order:  $UO_3 \cdot xH_2O$  > ammonium diuranate > sodium diuranate (Table 1.3).

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 (1.4).

**Table (1.4): 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 the following concluding remarks could be drawn:

1. The average mass concentration of uranium from Uro and Kurun rock phosphate falls within concentration characteristic for unconventional resources.
2. There is no remarkable isotopic fractionation of uranium isotopes observed during hydrometallurgical process as evident from their activity ratios.
3. The percent of uranium dissolution from the rock phosphate with  $H_2SO_4$  is very low (48%)
4. 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.
5. 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 that the further studies should consider the following:

1. The use stainless steel containers fitted with thermostat for temperature control in leaching process and more efficient filtration or centrifugation method to separate the leachate in order to avoid long retention time of slurry.
2. Precipitation of iron from the green phosphoric acid prior to precipitation of uranium in order to avoid co-extraction problem during TBP purification step.
3. Monitoring the pH of solution during leaching process is vital in avoiding complexation reactions which makes Fe unavailable for oxidation of uranium thus lowering its percentage of dissolution.

## **ACKNOWLEDGEMENT:**

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