

ANALYSIS OF URANIUM LEACHING PROCESS AND EFFECT OF CAKE WASHING ON URANIUM RECOVERY

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Abstract

Sulphuric acid is the most preferred leachant for the recovery of uranium from ores because it is cheap, less corrosive, and produces anionic uranyl complex, which makes the separation of uranium from other cationic gangue mineral easy using an anionic exchanger subsequently. Sulphuric acid leaching of Narwapahar (INDIA) uranium ore assisted with acoustic cavitation and without cavitation has been studied. The primary uranium minerals of Narwapahar ore are uraninite and pitchblende with minor presence of brannerite, allanite, xenotime, and davidite. In this paper, we have discussed selective leaching of uranium using sulphuric acid from Narwapahar uranium ore relative to other leachable compounds and material balance has been carried out around each of the leaching experiments. Material balance of uranium ore and also that of uranium leaching for with and without cavitation could be established within $\pm 10\%$.

Keywords and phrases: uranium, leaching, cake washing, acoustic cavitation.

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1. Introduction

Sulphuric acid leaching is the most commonly used practice for the recovery of uranium from its ores. The major disadvantages of nitric acid are (a) it dissolves considerable amount of gangue material along with uranium and (b) it is costlier than sulphuric acid. Hydrochloric acid is not preferred due to its highly corrosive nature. Though carbonate leaching is more selective, it is used mostly for treatment of ores, which contain higher acid consuming carbonate minerals. Kinetics of carbonate leaching is slow and also carbonate does not attack calcareous materials, which may be encapsulating uranium, necessitating fine grinding of ore to achieve reasonable leaching rate [1] adding to grinding energy cost. In general, carbonates are costlier than acid. Sulphuric acid reacts with hexavalent uranium and produces anionic uranyl sulphate complex, which makes its separation easy from other cationic gangue mineral in subsequent anion type ion exchange.

From geological data, it is known that uranium is as abundant as lead, about 4ppm, in the earth's crust. But because of the chemical reactivity of its ions and relative solubility of many of its hexavalent compounds in aqueous solution, it is found that uranium is widely dispersed and significant concentrations in the form of high grade deposits are exceptional or rarity.

Uranium ores can roughly be classified into five categories based on the chemical nature of the embedded uranium minerals and their response to leaching:

(1) Ores containing tetravalent uranium: Most of the world's important deposits contain a significant proportion of their uranium in the tetravalent form. The important examples of this type are primary minerals like uraninite, pitchblende, coffinite, and uranothorite.

(2) Ores containing hexavalent uranium: These minerals are the hydrated oxides like gummite, phosphates like autonite and torbernite and vanadates like carnotite and silicate.

(3) Refractory uranium minerals: These ores are characterized by their resistance to chemical attack. Davadite and brannerite are the examples of such ores.

(4) Carbon associated uranium ore: Uranium occurs as an organo complex in minerals.

(5) Phosphate associated uranium: Uranium is a common constituent of the phosphate rocks [2].

Narwapahar ore is uraninite type ore. Petrology of a lean uranium ore sample from Narwapahar is shown in Figure 1. Uranium is hosted in chlorite-sericite-quartz schist and feldspathic schist. Sulphides are very low in this deposit. The primary uranium minerals are uraninite and pitchblende with minor presence of brannerite, allanite, xenotime, and davidite. Two types of uraninite are found in ore, one is irregular particles and aggregates and the other as pore fillings in chlorite and sericite schists [3].

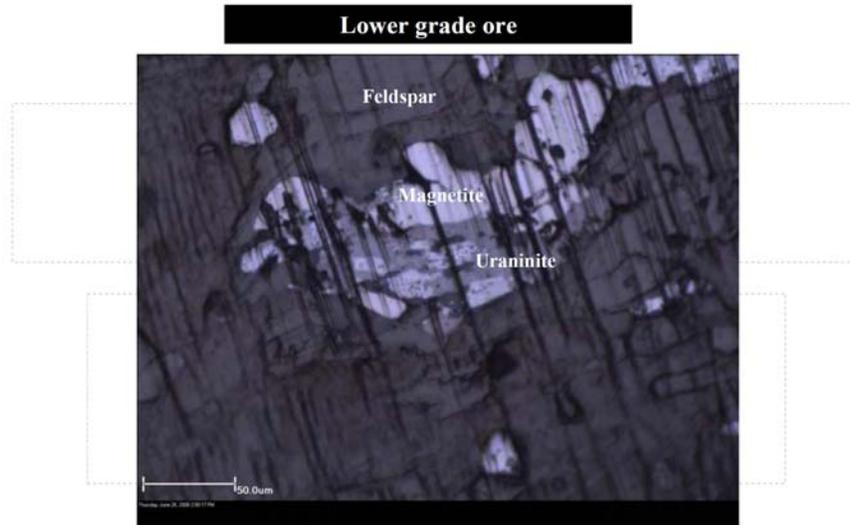


Figure 1. Narwapahar uranium ore: Petrography (reflected light).

2. Experimental Procedure

Uranium leaching experiments have been conducted with mechanical agitation (Experiment No. 1) and with acoustic cavitation supported mechanical agitation (Experiment No. 2 and 3). For Experiment 1 and 3, 30 μ m average particle size Narwapahar ore is used and 200 μ m average particle size Narwapahar ore is used for Experiment 2. Iron as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added at the beginning of Experiment 2 and 3, 465g and 410g, respectively. Experiments have been conducted under simulated plant conditions in a batch reactor having volume of 30 liter as shown in Figure 2.

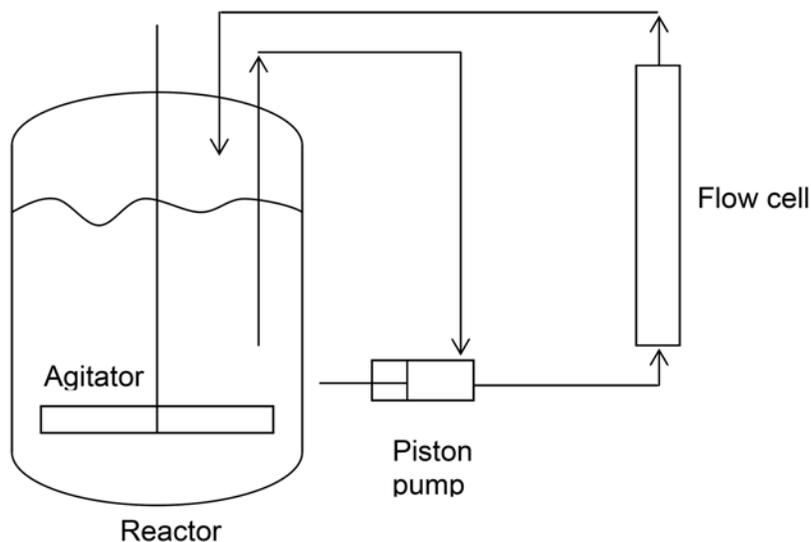


Figure 2. Experimental set up for ore leaching with acoustic cavitation.

The ore slurry was prepared by using ore and water. The ore slurry was kept in suspension using 4 pitched blades down pumping impeller (diameter 0.2m) rotating at 100rpm in the reactor. In case of Experiment 2 and 3, slurry was circulated through the ultrasonic flow cell using a piston pump at a rate of $1.5\text{m}^3/\text{hr}$, giving pipe slurry velocity of 0.8m/s ensuring no sedimentation during the hydraulic transport. Cavitation was generated by 1kW radial ultrasonic horn arranged as a flow cell. The concentrated H_2SO_4 and laboratory grade MnO_2 were added in a controlled manner in slurry mass to maintain required pH and oxidation reduction potential (ORP). The pH and ORP were monitored using pH and ORP probes. These probes were attached to a 2-channel display. The pH was maintained at 2.0 during initial 2hr of experiment and at 1.8 for the rest of leaching period. The ORP was maintained between 480-510mV during the experiment. At the end of experiment, slurry was discharged through bottom valve and collected in bucket. Leached liquor was decanted after settling of solid particles. Water washes were given to

the settled solids and the washings were filtered using Buchner funnel. The washing filtrate and residual solid was analyzed in addition to the leached liquor for uranium balance.

3. Analytical Methods

3.1. Uranium in ore and residue

Uranium content in the ore and residue samples have been carried out as per the procedure followed by UCIL [4]. Weighted quantity of sample is digested with hydrofluoric acid-nitric acid mixture and uranium in the resultant solution is extracted with tri-*n*-butyl phosphate diluted with kerosene. Uranium from the organic is stripped with sodium sulphate and the solution is made alkaline with sodium hydroxide. Colour development is achieved by adding hydrogen peroxide and the absorbance of this complex is measured at 380nm. The overall precision of this method is within $\pm 5\%$ for analyzing the uranium in ore and residue is also determined using bromo-PADAP as the colour forming reagent [5]. In this procedure, the sample is digested with a mixture of nitric acid-hydrofluoric acid and the uranium is extracted using tri-octyl phosphineoxide diluted with cyclohexane. Colour is developed in the organic phase using 1% solution of bromo-PADAP. Absorbance measurement is carried out at 574nm. The precision of this method is also within $\pm 5\%$.

3.2. Uranium in the leached liquor

Uranium in the leached liquor is measured by spectrophotometric method using dibenzoyl methane as the chromogenic reagent [6]. Uranium is extracted into ethyl acetate medium using aluminium nitrate as a salting out agent. Absorbance measurement is carried out at 395nm using 1cm cells. The precision of this method is known to be within $\pm 3\%$.

3.3. Uranium in the wash

The above methods were not used for determination of uranium in the wash due to low concentration of uranium in the wash. A sequential ICP AES (induction coupled plasma atomic emission spectroscopy) with a radial plasma and PMT detector is used for this purpose. Two interference free lines of uranium (385.465nm and 409.014nm) are used for determination. The precision of this method is within $\pm 5\%$.

3.4. Iron

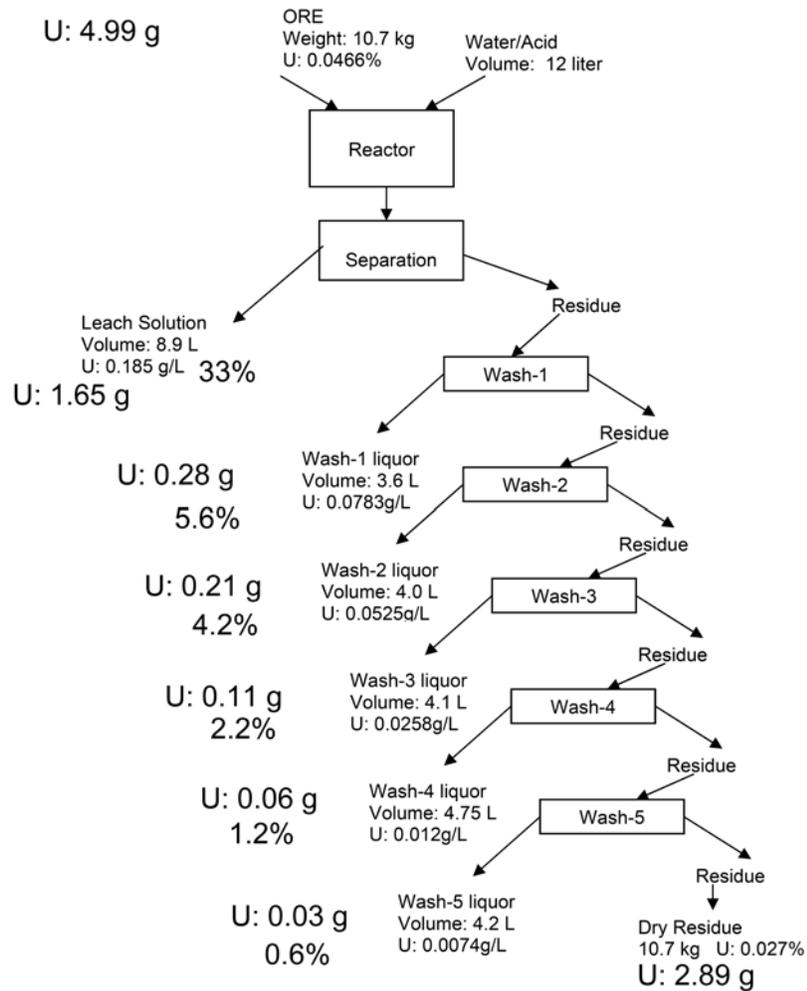
Iron content of all the samples is analyzed by o-phenanthroline spectrophotometric method. Absorbance measurements were measured at 515nm. The precision of the method is within $\pm 5\%$.

The determination of uranium in ore and residue samples were also carried out by neutron activation technique (NAA). For ore samples, the result of duplicate samples differed significantly. In the case of residue samples, the uranium values were found to be significantly less than that obtained by other methods used. The analysis of uranium in leached liquor did not match with uranium in leached liquor calculated based on ore and residue analyses by NAA. Considering all this drawback result of NAA is not used for material balance.

4. Results and Discussion

The material balance sheets show the uranium concentration and uranium content at different stages of processing as Figures 3-5. It can be seen from the material balance sheets that material balance is agreed within $\pm 10\%$ of uranium content in the ore. The unaccounted uranium for Experiment 1 is 4.81%, for Experiment 2 is 9.43% and for Experiment 3 is 9.36%. This is attributed to the error in sampling, analysis and handling loss during the experiments. Precision of analytical methods do not include sampling error. There is an uncertainty in obtaining representative sample of the ore and residue as the ore and residue are

solid powder. Considering the precision of different analytical methods used for uranium content estimation and sampling uncertainty the balance of uranium in all three experiments are quite satisfactory. Leaching efficiency for Experiment 1 is 48%, for Experiment 2 is 58%, and for Experiment 3 is 61% on basis of overall material balance. Significant uranium is recovered in washing in all experiments. Percentage recovery of uranium at each stage of washing is summarized in Table 1. Though average particle size of residue is 30 μ m for all experiments, the distribution of particle size is different. There is small peak in submicron range in Experiment 2 and 3; this peak shows the presence of finer particles. Recovery of uranium during washes is different in all three experiments and total recovery of uranium is varies from 10 to 20%. Balance of iron is summarized in Table 2. Unaccounted iron is less than 15% in these experiments. This unaccountability is due to sampling and analysis error as well as loss of material during experiments. Concentration of iron in ore is 11-11.25% and leaching of iron is less than 1% during experiments. Iron in washing was not analyzed and this has resulted in the increase of unaccounted iron. It has been observed that when iron concentration in the leached liquor is less, leaching of uranium is also less. More than 80% of iron added as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ has come out with the solid residue. This may be due to precipitation of iron during settling of slurry mass in settler. It has been observed that pH of decanted leached liquor is more than 3 even though pH is maintained during experiment is 1.8. Rise of pH may be due to consumption of acid by gangue minerals. These three experiments were conducted to establish the uranium balancing during leaching process.



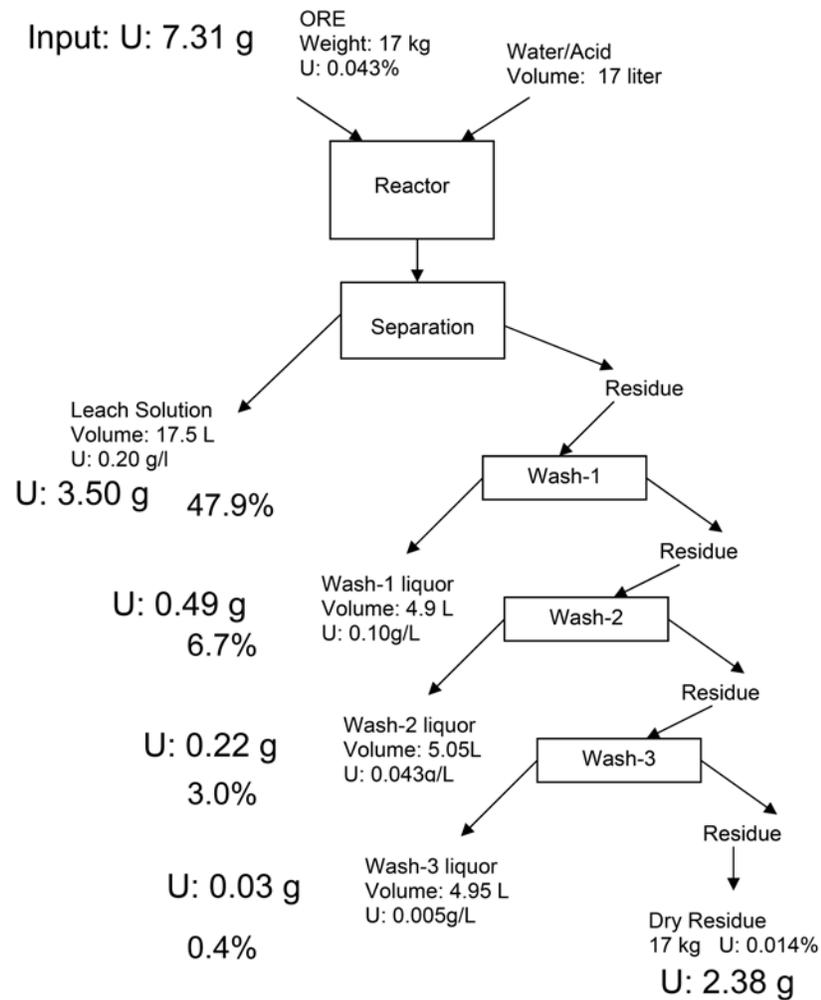
Input Uranium = 4.99g

Output Uranium = 1.65g + 0.28g + 0.21g + 0.11g + 0.06g + 0.03g
+ 2.89g = 5.23g

Unaccounted Uranium = 4.99g - 5.23g = - 0.24g

Percentage unaccounted Uranium = $\frac{-0.24}{4.99} = -4.81\%$

Figure 3. Material balance sheet for Experiment 1.



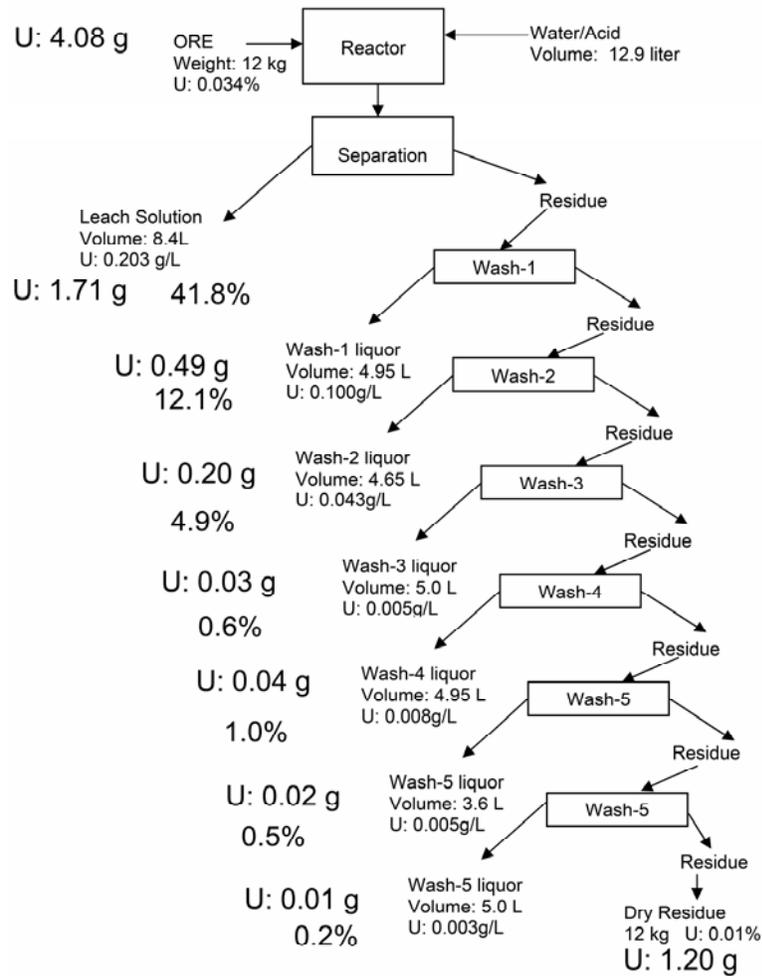
Input Uranium = 7.31g

Output Uranium = 3.50g + 0.49g + 0.22g + 0.03g + 2.38g = 6.62g

Unaccounted Uranium = 7.31g - 6.62g = 0.69g

Percentage Unaccounted Uranium = $\frac{0.69}{7.31} = 9.43\%$

Figure 4. Material balance sheet for Experiment 2.



Input Uranium = 4.08g

Output Uranium = 1.71g + 0.49g + 0.20g + 0.03g + 0.04g + 0.02g
+ 0.01g + 1.20g = 3.70g

Unaccounted Uranium = 4.08g - 3.70g = 0.38g

Percentage Unaccounted Uranium = $\frac{0.38}{4.08} = 9.31\%$.

Figure 5. Material balance sheet for Experiment 3.

Table 1. Recovery of uranium during washing at each stage

	Experiment 1	Experiment 2	Experiment 3
	% recovery	% recovery	% recovery
Leached Liquor	33	47.9	41.8
Wash 1	5.6	6.7	12.1
Wash 2	4.2	3.0	4.9
Wash 3	2.2	0.4	0.6
Wash 4	1.2	-----	1.0
Wash 5	0.6	-----	0.4
Wash 6	-----	-----	0.4
Total of wash	13.8	10.1	19.1

Table 2. Iron balance (without accounting for washes)

Experiment 1			
Input (g)		Output (g)	
Iron in ore	1204.8	Iron in residue	1167.0
Iron added as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.0	Iron in leached liquor	10.1
Total	1204.8	Total	1177.1
Difference in input and output		2.3%	

Experiment 2			
Input (g)		Output (g)	
Iron in ore	1912.5	Iron in residue	1740.8
Iron added as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	92.3	Iron in leached liquor	11.4
Total	2004.8	Total	1752.2
Difference in input and output		12.6%	

Experiment 3			
Input (g)		Output (g)	
Iron in ore	1320.0	Iron in residue	1584.1
Iron added as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	81.4	Iron in leached liquor	14.3
Total	1401.4	Total	1598.4
Difference in input and output		14.1%	

5. Conclusion

Material balance of uranium ore leaching is found to agree within $\pm 10\%$ of uranium content in ore. This is attributed to solid sample in homogeneity, to the material handling during experiment and washing inefficiency for finer. Methods used for analysis of various samples are found to suffice the purpose, in respect of their precision. Significant amount of uranium recovered in washing stages shows the importance of washing for uranium recovery from the leached out ore. Uranium recovered by washes is up to 19% of total input uranium. Material balance of iron in ore leaching operation is found to agree within 15% of input iron. Total recovery of uranium is 47%, 58%, and 61%.

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