Recovery of uranium from Tummalapalle leach solution using novel precipitating method

Sujoy Biswas
Uranium Extraction Division

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Abstract

The recovery of uranium from carbonate ore leach solution was studied using novel precipitation method. The uranium ore leached using Na_2CO_3/$NaHCO_3$ was recovered as magnesium di uranate (MDU) with excess NaOH in presence of trace amount of Mg^{2+}. The overall uranium recovery of the process was 97% with improved particle size (~57 µm). Based on the experimental findings, a process flow-sheet has been developed for the recovery of uranium from carbonate ore leach solution with a uranium concentration of < 1g/L.

Key Words: Uranium, Carbonate ore, MDU, Tummalapalle, Precipitation

Introduction

Nowadays nuclear power becomes an important resource of energy worldwide due to its several advantages over conventional energy sources [**1,2**]. In the development Nuclear Energy Programme, the uranium plays an important role as it is used as a primary nuclear fuel in nuclear reactor [**2,3**]. The sustainability of Nuclear Power Program depends on the availability of natural uranium in the front-end of nuclear fuel cycle along with established nuclear technology. In a country like India, only 3% of the total energy comes from the nuclear sources [**4**]. Considering shortage in the availability of fossil fuels and other resources of energy, the nuclear power may play as a big contributor in the total energy production of the country in near future. To meet such nuclear energy requirement, there is a need for constant supply of natural uranium which will come from various resources including lean sources like carbonate ore situated at Tummalapalle, India [**5, 6**]. The Tummalapalle has a vast deposit of uranium as carbonate ore in the host rock of alkali (dolomite and calcite) containing 0.048 % U_3O_8 and hence considered as lean resource of uranium [**7-8**]. The chemical composition of Tummalapalle ore was given in **Table 1 [8, 9]**. The recovery of uranium from such lean source becomes a challenge to the scientist and technologist working in the field of separation science and technology due to non availability of suitable recovery technique [**5**]. Generally, leaching of uranium from carbonate ore, Tummalapalle was carried out using alkali (Na_2CO_3/$NaHCO_3$) leaching process in an autoclave at high temperature and pressure [**7-10**]. The uranium from leach liquor was precipitated as sodium di uranate (SDU) in presence of excess NaOH at ~ 50-55 °C. The chemical reactions involving leaching and precipitation of uranium from Tummalapalle ore are given by the following chemical reactions:

Table 1: Mineralogical composition of the Tummalapalle uranium ore sample

Mineral	% Weight
Carbonates	83.2
Quartz + feldspar	11.3
Apatite	4.3
Pyrite	0.47
Chalcopyrite	0.05
Galena	Traces
Magnetite	0.15
Ilmenite + leucoxene	0.25
Iron hydroxide (goethite)	0.27
Pitchblende in association with pyrite	0.1
Total	100.0

$$UO_2 + \frac{1}{2}O_2 \rightarrow UO_3 \quad (1)$$

$$UO_3 + 3Na_2CO_3 + H_2O \rightarrow Na_4UO_2(CO_3)_3 + NaOH \quad (2)$$

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \quad (3)$$

$$2Na_4UO_2(CO_3)_3 + 6NaOH \rightarrow Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O \quad (4)$$

The pyrites and other sulphide minerals are also oxidized to sodium sulphate and solubilized in leach liquor during the alkali pressure leaching according to the following equations:

$$2Fe_2 + 7O_2 + 8\,Na_2CO_3 + 6H_2O \rightarrow 2Fe(OH)_2 + 4Na_2SO_4 + 8\,NaHCO_3 \quad (5)$$

The literatures reports indicate that, the uranium concentration in feed solution must be above 1.2 g/L for complete uranium precipitation using excess NaOH and the precipitate obtained has very small average particle size (7-9µm) which creates problem during filtration. Currently, the uranium concentration in the carbonate leach liquor is < 1g/L and it is impossible to recover all uranium from such lean leach solution using existing processes. Considering the importance of uranium and its vast deposit in Tummalapalle ore, it is important to develop an efficient, alternate precipitation method for recovery of uranium from such carbonate ore leach solution.The present study deals with the development of a new efficient precipitation method for uranium recovery from Tummalapalle ore leach solution containing 0.74 g/L U in feed solution. Based on the experimental results a process flow-sheet has been proposed for recovery of uranium from Tummalapalle carbonate ore leach solution using $MgSO_4$ as a coagulant in presence of NaOH.

Experimental

Reagents and chemicals

Sodium Hydroxide (A.R. grade, 99% pure), Magnesium Oxide (Industrial grade), Magnesium Sulphate (L.R. grade 98% pure), poly vinyl chloride (E-Merk, > 97% pure), Tetrahydrofuran (E-Merk, > 97% pure) were used without any further purification. The alkaline ore leach solution containing 0.74 g/L U was obtained from Uranium Corporation of India Limited, Tummalapalle, India. All the other reagents used in the experiments were of A.R. grade. **Table 2&3** showed the specification of alkaline ore leach solution used throughout the experiments.

Table 2: Major composition of ore leach solution

Parameter	Value
[U]	0.74 g/L
pH	9.1
Specific gravity	1.14
TDS	154.72 g/L
SO_4^{2-}	69.66 g/L
CO_3^{2-}	13.79 g/L
HCO_3^-	18.23 g/L
F-	16 µg/mL

Table 3: Elemental composition of ore leach solution

Elements	Concentration, µg/mL
Fe	12
Al	31
Cr	<1
Mg	10
Mn	<1
Ni	<1
B	12
Cd	<0.12
Co	<0.12
Ce	<0.12
Sm	<0.12
Gd	<0.12
Dy	<0.12
Sr	<0.12
Eu	<0.12
Y	<0.12
Yb	<0.12

(5) (4)

Instruments

Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP OES, Model No. JY 238) was used for determination of uranium and other trace impurities in various samples. Laser Diffraction Particle Size Analyzer from CILAS (Model No. CILAS 1064 Liquid) was used for particle size analysis of uranium precipitate. A Thermo-Orion make pH meter containing Ross make glass electrode was used to monitor pH of the solution.

Experimental procedure

The uranium precipitation from carbonate leach solutions was investigated at different experimental conditions to obtain best suitable condition. The concentration of U(VI) in carbonate leach liquor was kept constant at 0.74 g/L. The precipitation reaction was carried out in batch mode in 5 L glass reactor containing 4 L carbonate leach solution. The glass reactor contains a marine type 3 bladed propeller for mixing of solution, constant temperature heater, thermocouple, digital temperature controller. The addition of chemicals such as MgO, $MgSO_4$ etc.were carried out in solid form in the leach liquor whereas addition of alkali (NaOH) was carried out in slurry mode. The solution mixture was stirred at constant r. p. m (300) for a period of 1 hour. The 5 mL samples were withdrawn from the glass reactor with the help of glass pipette at different time intervals for checking the pH and uranium concentration of the solution. The completion of the reaction was assured by checking the concentration of uranium in the filtrate. After completion of precipitation reaction, the

uranium slurry was filtered under vacuum and cake was dried in an oven at 110 ºC.

Results and discussions

The precipitation of uranium from carbonate ore leach solution was investigated in presence of $MgSO_4$ for recycling the excess reagents Na_2CO_3/NaOH in the leaching step. Variation of NaOH as well as temperature showed that only at 50 g/L NaOH concentration, above 55 °C, the uranium was precipitated as MDU in presence of $MgSO_4$. Further, it was observed that 1g/L $MgSO_4.7H_2O$ is required for effective recovery of uranium (97%) from carbonate leach solution containing 0.74 g/L U. The Mg^{2+} acts as a coagulant for uranium precipitation even in the carbonate /bicarbonate medium in presence of excess NaOH. The uranium precipitated as MDU has improved particle size distribution with the mean particle diameter of 57 µm (**Table 4**). The MDU precipitate was filtered and washed with hot water to remove any carbonate, bicarbonate and sulphate present as impurities. The MDU was dried at 110 ºC in an oven and analyzed for % uranium content and % un-dissolved after dissolving in HNO_3 medium. It was found that, the MDU cake contained50% uranium with less than 1% un-dissolved substance (**Table 5**). The Filtrate from filtration of MDU cake was subjected to freeze crystallization to remove sulphate as solid Na_2SO_4 at 0 ºC temperature. After freeze crystallization, the solution was analyzed for Mg^{2+} content for five consecutive batches and it was found that the Mg^{2+}concentration in every case was < 0.5 µg/mL.Since the filtrate after Na_2SO_4 removal contains only Na_2CO_3 and NaOH, the reagent (filtrate) can be recycled for leaching of uranium after passing CO_2 and adjusting proper composition of leaching agent.

Table 4: Particle size analysisof MDU cake prepared from carbonate leach solution using NaOH/$MgSO_4$; $MgSO_4.7H_2O$: 1 g/L; T: 55 ºC; NaOH: 50 g/L; Stirring speed: 300 r.p.m; $[U]_{feed}$: 0.74 g/L.

Diameter at 10%	20.91 µm
Diameter at 50%	52.52 µm
Diameter at 90%	103.05 µm
Mean diameter	57.47 µm

Table 5: Analysis of MDU cake prepared from carbonate leach solution using NaOH/$MgSO_4$; $MgSO_4.7H_2O$: 1 g/L; T: 55 ºC; NaOH: 50 g/L; Stirring speed: 300 r.p.m; $[U]_{feed}$: 0.74 g/L.

% U (dry basis)	% Un-dissolved
50	<1

Process flow-sheet for uranium recovery

Based on experimental results an optimized process flow-sheet has been proposed for recovery of uranium from carbonate leach solution containing < 1 g/L U (**Figure 1**). The carbonate ore containing uranium was crushed and ground and the ground ore was taken in a leaching tank containing Na_2CO_3/$NaHCO_3$ mixture as leaching reagents. The leaching of uranium was performed under high pressure and temperature (140 ºC). After leaching reaction was over, the solid –liquid separation was performed where leach liquor containing uranium was separated from solid residue. The pH of the leach liquor was ~9 with a uranium concentration of 0.74 g/L. In a precipitation reactor, 1g/L $MgSO_4$.7H2O was added in solid state in leach liquor with constant stirring. The solution was heated up to 55 ºC and excess NaOHslurry was added to it with constant stirring. The solution was left as it is for a period of 1 hour to complete the precipitation. The uranium in presence of NaOH/$MgSO_4$ mixture was precipitated as MDU cake with large particle size (mean particle diameter ~57µm). Further, the MDU cake was filtered and washed with hot water to get pure MDU cake which was dried at 110 ºC. On the other hand, filtrate containing excess NaOH, Na_2CO_3 and Na_2SO_4 need to be separated for further reuse. The filtrate after precipitation undergoes freeze crystallization where Na_2SO_4 was removed as solid cake. Now the filtrate containing excess NaOH and Na_2CO_3 can be recycled for leaching as Na_2CO_3/$NaHCO_3$ after passing CO_2 through the solution.

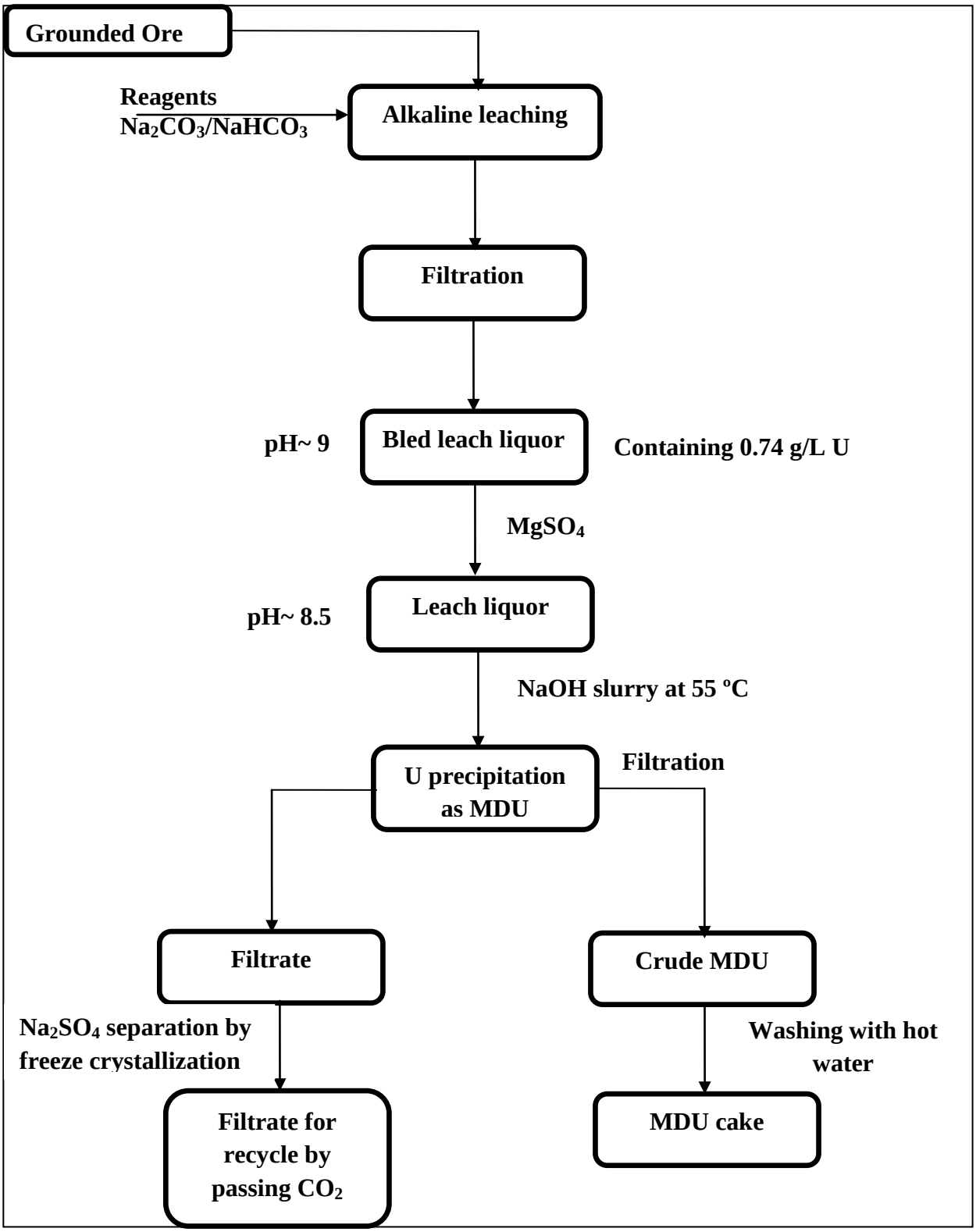

Figure 1:Process flow-sheet for the recovery of uranium from carbonate ore (Tummalapalle, India) leach solution using $NaOH/MgSO_4$ mixture

Conclusions

Recovery of uranium from carbonate ore leach solution containing 0.74 g/L U was studied using excess NaOH in presence of Mg^{2+}. The precipitation of uranium from carbonate leach solution was also possible without addition of any acid when NaOH was used as precipitating agent and $MgSO_4$ as a coagulant at high temperature (50-55 ºC). With increase in Mg^{2+} concentration in the medium, there is an increase in particle size of MDU during precipitation. Based on the experimental findings, a process has been finalized for uranium recovery from Tummalapalle carbonate ore leach solution using NaOH/$MgSO_4$ mixture at 55 ºC. The MDU cake contains 50 % U and filtrate can be recycled in uranium leaching after separation of sulphate as solid Na_2SO_4 using freeze crystallization.

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References

1. B. Bhattacharjee, An overview of R&D in fuel cycle activities of AHWR, 14th Indian Nuclear Society Annual Conference (INSAC), IT-1 (**2003**) 1-27.
2. T.K. Mukherjee, H. Singh, 14th Indian Nuclear Society Annual Conference (INSAC), IT-7 (**2003**) 1-9.
3. A. Kakodkar, Evolving Indian Nuclear Power Programme: Rationale and Perspective, Nuclear India, 41 (11-12) (**2008**).
4. Integrated Energy Policy: Report of the Expert Committee. Planning Commission Document, Government of India, (**2006**) p.1-147.
5. N.P.H, Padmanabhan and A. K. Suri, Challenges in augmenting the uranium supply position in India, International Seminar on Mineral Processing Technology ((**MPT-2007**), Mumbai, India, pp 3-18.
6. A.K. Rai, S. Zakaulla, AnjanChaki, Proterozoic stratabound carbonate rock (dolostone) hosted uranium deposits in Vempalle formation in Cuddapah basin, India, International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle (**URAM-2009**) 22-26 June **2009**, Vienna, Austria.
7. A.K. Suri, Uranium Processing-A New Alkaline Route, Transaction of Indian Institutes of Metals, 61 (1) (**2008**).
8. A.K. Suri, S.K. Ghosh and N.P.H, Padmanabhan, Recent pilot-plant Experience On Alkaline Leaching of low Grade Uranium Ore in India, International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle (**URAM-2009**) 22-26 June **2009**, Vienna, Austria.
9. A.K. Suri, T. Sreenivas, Developments in processing of conventional uranium ore resources of India, 6th International Mineral Processing Conference (IMPC), New Delhi, India, October, 2012.
10. A.K. Suri, N.P.H. Padmanabhan, T. Sreenivas, K. Anand Rao, A.K. Singh, K.T. Shenoy, T. Mishra, S.K. Ghosh, Process development studies for low-grade uranium deposit in alkaline host rocks of Tummalapalle, Presented at IAEA Technical Meeting on low-grade Uranium Deposits at Vienna, 29-31 March, 2010.
11. S. Bachmaf, B. Planer-Friedrich and B.J. Merckel, Radiochim. Acts. 96 (2008) 359-366.
12. B. Tomazic, M. Samarzija, J. Inorg. Nucl. Chem. 31 (1969) 1771–1782.
13. B. Tomazic, M. Branica, J. Inorg. Nucl. Chem. 34 (1972) 1319–1332.
15. R.M. Rush, J.S. Johnson and K.A. Kraus, Inorg. Chem. (1) (1962) 378
16. B. Tomazic, M. Branica and B. Tezak, Croat.Chem. Acta. 34 (1962) 41