

Recovery of Uranium from Alkaline Ore Leach Solution Using a Precipitating Method

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Abstract: In this paper, recovery of uranium from carbonate ore leach solution has been reported using a novel precipitation method. The method is based on the precipitation of uranium as yellow color magnesium diuranate (MDU) using MgO/NaOH mixture. The process has been finalized by optimizing various process parameters such as concentration of CO_3^{2-} , HCO_3^- , HCl, NaOH, MgO and reaction temperature. The overall recovery of uranium was 97%. The chemical composition of the yellow precipitate (MDU) was evaluated employing XRD technique. A process flow-sheet has been developed for recovery of U(VI) from low concentration carbonate ore leach solution.

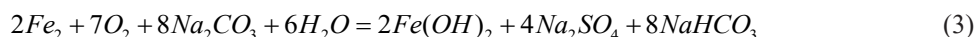
Keywords: uranium, carbonate ore, leaching, MDU, XRD

1. Introduction

Uranium is extremely useful element for the development of nuclear energy due to its use as a nuclear fuel in nuclear reactor. The nuclear fuel cycle states with the mining of uranium from earth crust, fuel fabrication, spent fuel reprocessing and end with the safe disposal of nuclear waste. In a developing country like India, the nuclear power plays an important role for long term energy security and economic development of the country since India has shortage of fossil fuels^[1-3]. Currently, only 3% of total energy has come from nuclear contribution and 25% nuclear contribution is expected in 2050 to sustain the GDP growth in the range of 8-10%^[4]. The increasing demand of nuclear power in India has triggered interest in the exploration of various resources of natural uranium including lean sources like carbonate ore situated at Tummalapalle, India^[5]. Further, the deposit of Tummalapalle is lower grade (~0.042% U_3O_8) but reasonably large reserve and it is confined in the host rock of alkali (dolomite and calcite). The Tummalapalle ore deposit becomes important due to its large amount of uranium content^[6]. At present, the recovery of uranium from Tummalapalle ore is carried out using alkaline leaching process where the ore is leached with a mixture of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ in presence of air at elevated pressure and temperature in an autoclave^[7-8]. Finally the uranium in leach liquor is precipitated with NaOH solution as sodium diuranate (SDU) at high temperature as per following chemical reactions^[8]:



The pyrite and other sulphide minerals present in the alkaline ore are also oxidized to sodium sulphate and solubilized in the reaction medium during alkaline pressure leaching according to following equation:



For complete precipitation, the minimum concentration of uranium in feed solution must be 2.4 g/L^[9-10]. Currently, the concentration of uranium in feed solution is < 1 g/L and it is not possible to precipitate the uranium as SDU completely using the existing process. Further, the mean particle size of SDU in the existing process is very less (6-8 μm) which creates difficulty in settling and filtration of SDU cake. Considering vast deposit of uranium in Tummalapalle ore, it is important to develop an alternate chemical process for complete recovery of uranium from such lean solutions. The aim of

the present study is to develop an efficient chemical process for the recovery of uranium from such ore leach solution containing < 1 g/L of uranium. In our earlier work, we have demonstrated an improved precipitation method for recovery of uranium from carbonate solution as MDU without any addition of acids ^[11]. In the present study uranium from Tummalapalle ore leach solution ([U]: 0.74 g/L) is precipitated as magnesium diuranate (MDU) in presence of MgO/NaOH mixture at 50°C. The main focus of the present work is the mechanism of uranium precipitation as MDU from carbonate leach solution. The pH of leach liquor was adjusted from 9 to 7 and requisite amount of MgO was added to the solution. Further, excess amount of NaOH was added in the solution to precipitate all uranium as MgU₂O₇ at pH ~12.5. The average particle size of the MgU₂O₇ particles was 20 µm and overall uranium recovery of the process was 97%. The composition of final precipitate was characterized using X-ray diffraction (XRD) technique. The present process was compared with the earlier one, SDU process and it was observed that the present process has high efficiency with improved average particle size distribution.

2. Experimental

2.1 Reagents and chemicals

Sodium hydroxide (A.R. grade, 99% pure), magnesium oxide (Industrial grade), poly vinyl chloride (A.R. grade, > 97% pure), tetrahydrofuran (A.R. grade, > 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 1 & 2 showed the specification of alkaline ore leach solution used throughout the experiments ^[11].

Table 1. Major composition of ore leach solution

Parameter	Value
[U]	0.74 g/L
Specific gravity	1.14
Total dissolved solid	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 2. Elemental composition of ore leach solution

Elements	Concentration, µg/mL
U	740
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

2.2 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 cake. A Thermo-Orion make pH

meter containing Ross make glass electrode was used to monitor pH of the solution. X-ray diffraction spectrophotometer (SIEMENS D-5000) was used in the present study for chemical compositional characterization of uranium cakes. The X-ray diffraction of the samples were performed using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) using a few milligram of a sample placed in a sample holder. The samples were mounted in a glass plate with the help of a solution of polyvinylchloride in Tetrahydrofuran. A step size of 0.02 for 2θ and a speed of 0.3°/min were used for the analysis.

2.3 Experimental procedure

The precipitation reaction was carried out in batch mode using 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 was 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 rpm (600) for a period of 1 hour. 5 mL samples were withdrawn from the glass reactor with the help of glass pipette at different time intervals for checking the 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°C for a period of 3 hours.

3. Results and discussions

3.1 Effect of addition of hydrochloric acid

Table 3. Effect of HCl on uranium recovery from carbonate leach solutions.
NaOH: 20 g/L; T: 25°C; [HCl]: 11 M; Stirring speed: 600 rpm; [U]feed: 0.74 g/L

Volume of HCl, mL/L	[U] _{filtrate} , µg/mL	% U Recovery	Mean diameter, µm
75	46	93.78	10
100	38	94.86	12
125	20	97.29	16
150	26	96.48	20

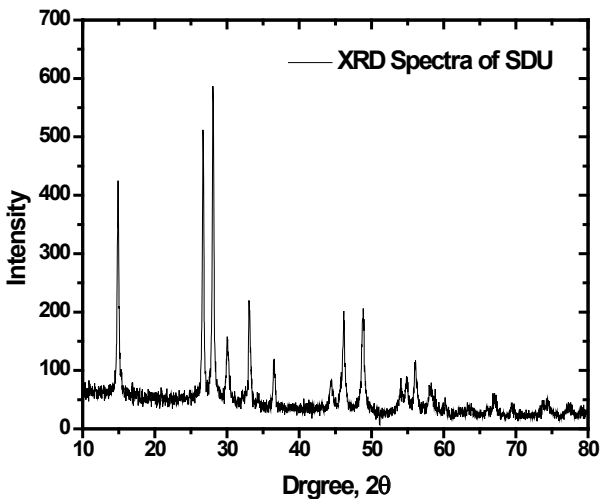


Figure 1. XRD profile of sodium diuranate (SDU) precipitated from carbonate leach solution using NaOH

Literature data indicates that the uranium from carbonate leach solution was generally precipitated as yellow color SDU using NaOH at 40-50 °C according to equation 2. The average particle size of the SDU precipitate is in the range of 6-8 µm which create problem in settling the yellow cake at the bottom of the reactors^[9,10,12]. Further, it is reported that if the uranium concentration goes below a minimum value (2.4 g/L), complete precipitation of uranium is not possible and most of the SDU particles remain in solution as colloidal state. Currently, the uranium concentration in Tummalapalle leach liquor is 0.74 g/L with the presence of other anions 69.66 g/L SO₄²⁻, 13.79 g/L CO₃²⁻ as well as 18.23 g/L HCO₃⁻ and NaOH it fails to precipitate uranium completely as SDU. The presence of complexing anion, CO₃²⁻ prevents the precipitation of uranium from carbonate leach solution when the uranium concentration goes below 2.4 g/L. To reduce the effect of CO₃²⁻, HCl is added in carbonate leach solution and its pH is reduced from 9.1 to ~7 where most of the carbonate converts to bicarbonate. According to pourbaix diagram at pH ~7, U(VI) mainly exist as (UO₂)₃(OH)₅⁺ and trace

amount of $\text{UO}_2(\text{CO}_3)_3^{2-}$ and at $\text{pH} > 8$ U(VI) exist as a mixtures of $\text{UO}_2(\text{CO}_3)_3^{2-}$ and $\text{UO}_2(\text{CO}_3)_4^{4-}$ [12-14]. After conversion of $\text{UO}_2(\text{CO}_3)_4^{4-}$ complex to $(\text{UO}_2)_3(\text{OH})_5^{+}$, 25 g NaOH slurry was added in 1 L of leach solution with constant stirring at 25°C. A yellow color precipitate was obtained with the average particle size of 10 μm and the overall uranium recovery was ~93% (Table 3). XRD study showed that the yellow precipitate was sodium diuranate (SDU) (Figure 1). With increase in amount HCl from 75 mL/L to 125 mL/L there was an increase in uranium recovery from ~93 % to 97 % as well as mean particle diameter from 10 to 16 μm . Further rise in acid volume/concentration, there is no increase in overall uranium recovery of the process, although there is an increase in average diameter of SDU particles. The increase in particle size of SDU is due to the decrease in carbonate as well as $\text{UO}_2(\text{CO}_3)_4^{4-}$ ions concentration in the reaction medium which accelerate the agglomeration of primary particle formed during precipitation of uranium.

3.2 Effect of MgO

The effect of MgO on uranium recovery was studied for obtaining large particle size of precipitate by spending minimum amounts of chemicals. With increase in MgO concentration in reaction medium, there was an increase in efficiency of the process as well as particle size of the uranium cake (Table 4). The uranium precipitation reaction follows in two steps forming final compound, MDU at $\text{pH} \sim 12.5$. In the first step, addition of HCl will destroy the $\text{UO}_2(\text{CO}_3)_4^{4-}$ complexes present in the solution at $\text{pH} < 7$. In the next step, addition of MgO in reaction medium at $\text{pH} \sim 7$ leads to formation of Mg^{2+} through hydration which acts as a coagulant for uranium precipitation. The hydration of MgO at neutral pH is proceeding through following equations [15]:

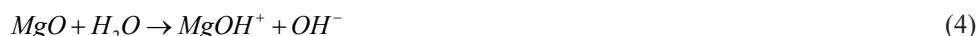
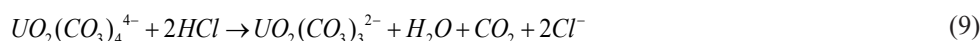


Table 4. Effect of addition of MgO on uranium recovery from carbonate leach solutions.
NaOH: 20 g/L; T: 25 °C; [HCl]: 11 M; Volume of HCl: 75 mL/L; Stirring speed: 600 rpm; [U]feed: 0.74 g/L

[MgO], g/L	[U] _{filtrate} , $\mu\text{g/mL}$	% U Recovery	Mean diameter, μm
0.5	41	94.50	9.74
1	37	95	12
1.5	33	95.54	18

Further, the addition of NaOH in solution will lead to increase in pH of the reaction medium leading to complete precipitation of uranium as yellow color magnesium diuranate (MDU). The precipitation of uranium in hydroxide medium proceeds through formation of negative charge colloid particles called primary particles. The addition of NaOH will increase HO^- ions in the solution forming negative charge colloid particles having various chemical compositions. The whole processes for U(VI) precipitation from carbonate leach solution can be presented by the following steps [16-18]:

Step (1)

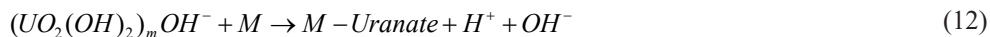


After addition of NaOH:

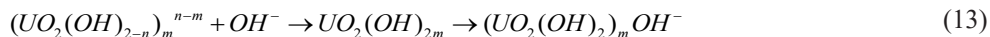
Step (2)



Step (3)



Step (4)



Step (5)



Where M represents the cation present in the medium.

Step (1) represents the formation of less complexing HCO_3^- ions from more complexing CO_3^{2-} ions by adding HCl. On the other side, at pH~7, the highly stable complex, $UO_2(CO_3)_4^{4-}$ converts in to $UO_2(CO_3)_3^{2-}$ and $(UO_2)_3(OH)^{5+}$ [12-14]. Step (2) shows the formation of U(VI)-hydroxo complexes, where “m” describes the degree of polymerization. Rush et al. [19] observe by ultracentrifuge measurement that the dimer is the predominate species and polymerization does not exceed three. Further interaction of polymers with hydroxide ions lead to the formation of metastable colloid particles of uranyl hydroxide which is negatively charged in nature as shown in step (3) [20]. The stability of colloid is highly sensitive to the presence of neutral electrolytes and its charge on the cations or anions opposite to the charge of colloidal particles. The transition of solute species into the solid phase consists of five subsystem (i) formation of various complexes, (ii) embrionation, (iii) nucleation (iv) micellation (formation of primary particles) and (v) secondary aggregation. The role of Mg^{2+} is to bring the small negative charge primary particles (micelles) together to form bigger particles/agglomerates (secondary aggregation). Since, such kind of phenomena called coagulation depends on the charge of the cation and its concentrations, with increase in cationic charge or concentrations will lead to increase in formation of bigger agglomerate due to more coagulation (agglomeration). Step (4) represents the phenomena of coagulation of negatively charged colloidal particles in presence of metal ion (Mg^{2+}). In alkaline medium the excess HCO_3^- is converted in to CO_3^{2-} in presence of NaOH (Step 5). Tomazic et al. [17] observe that the presence of high charge cations such as Ba^{2+} and La^{3+} during precipitation of uranium with ammonia as ammonium di uranate (ADU) leads to increase in precipitation rate and formation of bigger ADU particles.

3.3 Effect of temperature

The variation of temperature is an important parameter for controlling the kinetics of a precipitation reaction. The effects of temperature on uranium precipitation from carbonate leach solution were investigated by varying temperature of the reaction mixture from 25°C to 50°C. With increase in temperature of the reaction mixture, there was an increase in uranium recovery as well as mean particle size of the uranium cake (Table 5). The precipitation of uranium in presence of MgO/NaOH mixture has occurred through formation of small charged, colloid particles called primary nucleus. With rise in temperature of the system, the velocity of the primary nucleus increases as per Boltzman distribution law leading to rise in collision frequency among the primary nucleus. The increase in collision among the primary nucleus increases the probability of bringing the more number of primary nucleuses together to form bigger particle leading to precipitation from the medium. Further, in order to understand the effect of temperature on precipitation of MDU, we need to consider the simplified precipitation mechanism in terms of nucleation and agglomeration (crystal growth). As mentioned in the previous section, the precipitation of MDU proceeds through various chemical reactions (equations 11-13) and to effect nucleation, it is necessary that the solution must be supersaturated. In case of MDU precipitation, a large number of nucleons collide to each other to form agglomerate. So, the formation of MDU agglomerate in such case can be explained in terms of rates of reaction in solution considering two steps (a) problems of encounter rates of nucleus and (b) available activation energy for agglomeration. Now, the encountered particles have two options, either to form agglomerate or to disperse. The overall process can be represented by the following equations:



Where X_1 and X_2 represent the different kind of nucleons (primary particles) and K_1 represents the rate of

agglomeration (crystal growth) ^[21]. Two cases may be arising. In first case, if the rate of dispersion is slow than agglomeration i.e. $K_1 \gg K_d$, then the rate of agglomeration will be high. In second case, if the activation energy (E_a) for agglomeration is high, then the rate of agglomeration will be temperature depended. In case of MDU formation, then the rate of agglomeration will be temperature depended. In case of MDU formation, the increase in the agglomeration (particle size) with temperature may be due to involvement of high activation energy during precipitations. Similar results have been observed during precipitation of ADU from uranyl nitrate solution using gaseous ammonia at low gas flow rate ^[21].

Table 5. Effect of temperature on uranium recovery from carbonate leach solutions.
NaOH: 20 g/L; [HCl]: 11 M; Volume of HCl: 75 mL/L; [MgO]: 0.5 g/L; Stirring speed: 600 rpm; [U]_{feed}: 0.74 g/L

Temperature, °C	[U] _{filtrate} , µg/mL	% U Recovery	Mean diameter, µm
25	41	94.50	9.74
35	30	94.94	11
45	22	97	17
48	21	97.16	22
50	15	97.97	25

3.4 XRD analysis of uranium cake

The uranium precipitate prepared from carbonate ore leach solution using NaOH and MgO/NaOH mixture have been studied for phase identification using X-ray diffraction technique. Figure 1 showed the XRD profile of uranium cake prepared using NaOH and it was found to be sodium diuranate (SDU). Figure 2 showed the XRD profile of uranium cake obtained with the help of MgO/NaOH mixture. The XRD peaks at diffraction angles at (2θ): 25.14°, 34.88°, 44.37° as well as 55.30° indicates that the yellow precipitate is magnesium diuranate (MDU). The experimental results showed that the presence of different cations influenced not only the particle size but also the composition of uranium cake. Further, it was observed that the nature as well as charge of cation determined the fate of the negative charge colloid to form precipitate (equation 13). In absence of any Mg^{2+} , the Na^+ will combine with negative charge colloid to form SDU, where as in presence of Na^+ and Mg^{2+} , the Mg^{2+} will combine with negative charge colloid to form MDU. The reason behind formation of MDU in presence of MgO/NaOH was because of high positive charge of Mg^{2+} compared to Na^+ leading to coagulation of negative charge colloid particles.

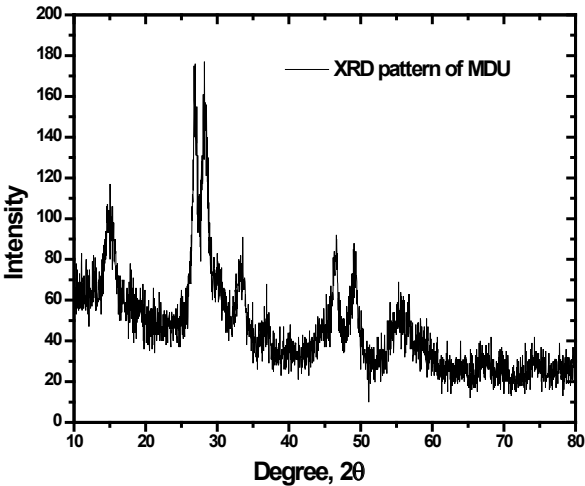


Figure 2. XRD profile of magnesium diuranate (MDU) precipitated from carbonate leach solution using MgO/NaOH

3.5 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 < 1g/L U (Figure 3). The carbonate ore was crushed and ground and the ground ore was taken in a leaching tank containing Na₂CO₃/NaHCO₃ mixture as leaching reagents. The leaching of uranium was performed under high pressure (9 Kg/cm² with oxygen partial pressure 5 Kg/cm²) and temperature (135-140°C). At this temperature and pressure, the leaching efficiency was found to be ~80%. 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 containing leach liquor, HCl was added in controlled manner until the pH comedown to ~ 7 . After acid addition, the solution was heated up to 50 °C and MgO/NaOH mixture 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 MgO/NaOH mixture was precipitated as MDU yellow cake with large particle size (mean particle diameter $\sim 25\ \mu\text{m}$). Further, the MDU cake was filtered and washed with hot water and dried at 100 °C. On the other hand filtrate containing excess NaOH 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 can be recycled for leaching as Na_2CO_3 after passing CO_2 through the solution.

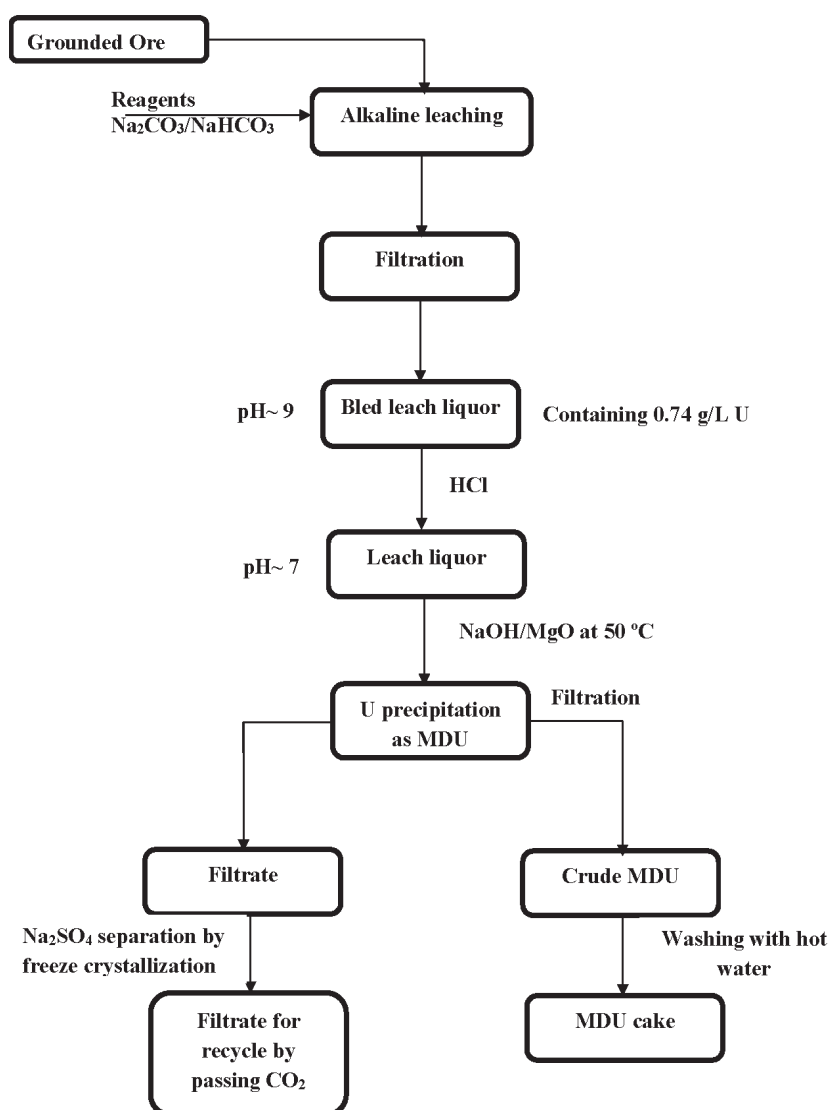


Figure 3. Process flow-sheet for the recovery of uranium from carbonate ore (Tummalapalle, India) leach solution using MgO/NaOH mixture

4. Conclusions

Recovery of uranium from carbonate leach solution was investigated using a novel precipitating method. The method was based on the removal of carbonate/bicarbonate from the solution using HCl and precipitation of uranium as MDU using MgO/NaOH mixture at pH 12.5. The XRD study showed that the uranium was precipitated as MDU. The particle size of MDU increased with increased in amount of MgO as well as with temperature. Based on experimental results a process flow-sheet has been proposed for recovery of uranium from carbonate leach solution.

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Conflicts of interest

The authors declare no conflicts of interest in this research.

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