

Alkaline Leaching of a Uranium Metal from the Ore Using EDTA

S.Purushotham, P. Bhavya Manjeera, P.J.Rao

Mineral Processing Engineering, Department of chemical Engineering, Andhra University College of Engineering
(A), Andhra University, Visakhapatnam, Andhra Pradesh, India,
Corresponding Email: purushotham.1141@gmail.com

Abstract: This paper deals with the leaching studies on a calcite ore containing radioactive element (U) in low concentrations. Uranium distributed in the ore in very wide range but it is very low concentrations. Recovery of Uranium in economical way is the primary requirement. Ore itself contains more amount of carbonate content so we have used alkaline leaching which is very economical. Ore samples of four different grades from the same deposit have been investigated for the leachability of radioactive metal. The radioactive metal concentrations of the ore samples studied are: Sample A, B, C and D assaying 179 ppm, 250 ppm, 392 ppm and 414 ppm respectively. The ore of particular grade was ground to 60% passing 75 μ sizes. Alkaline leaching of the ground ore was carried out in two stages. The first stage was carried out with sodium carbonate and sodium bicarbonate along with aeration at atmospheric pressure and 70°C for 6 hr. The residual cake after filtration was subjected to second stage of leaching using EDTA solution for 3 hr., 50% solids (by wt.), atmospheric pressure and 70°C in an attempt to increase the yield of the metal. The two stage leaching was carried out for four ore samples of different grades. The ore gangue constitutes a reactive component, pyrite, which also undergoes leaching. Hence, its concentration also monitored along with that of desired metal. The two stage leaching process tested in this study has yielded maximum of 58% recovery of metal into the leach liquors of both stages.

Keywords— Uranium, Alkaline leaching, Rod mill, EDTA, sodium carbonate and sodium bicarbonate, solid- liquid separation.

I. Introduction

Strategic and energy critical elements research and development as well as production are of national interest at present. The radioactive element for recovery of which, the experiments were carried out comes under this category. Also, processes must be developed for economical production of the metals and continuous research and development must be backed up due to rapid development of engineering and technology, which helps us to sustain in the world market. The paper is a part of research and development of the existing conventional flow sheet for the recovery of metal from Calcite based Indian ore. In general mineral processing flow sheet we will find comminution, leaching, solid liquid separation, liquor purification, precipitation of dissolved metal and effluents processing.

In this study alkali leaching was selected as it is suitable for the ore. The salient features of alkaline leaching are [1]

A. Reagents used are sodium carbonate and sodium bicarbonate.

B. Most metal carbonates are insoluble in water and don't form complexes

C. Stability of required metal complexes is high and selective dissolution from host ore matrix is the characteristics for the selection of alkaline leaching process.

D. Advantageous for processing ores with high CO_3^{-2} - mineral content. Because, the acid consumption will be more for carbonate rocks.

E. Relatively pure product is possible.

F. Reagents consumption is low and solutions are relatively non-corrosive.

In conventional flow sheet leaching operation was done at 125°C and 7.5 bar in presence of Oxygen. This is required to crack or decompose Iron pyrite, as the radioactive element of our interest is intricately trapped in the crystal lattice of pyrite. Breaking of pyrite is possible only at elevated temperature and pressure. Also, conversion of tetra-valent to hexavalent is necessary for the radioactive element for leaching to take place as the mineral of the element is present in both valencies. Succeeding operations in the flow sheet, purification and precipitation were not covered in this paper.

The mineralogical composition of the exploratory mine ore sample used for the flow sheet development work indicate presence of 83.2% by weight of carbonate minerals. Siliceous minerals in the ore are quartz, feldspar and chlorite (13%). Collophane (4%) is the only phosphate bearing phase. Pyrite is the predominant sulphide ore mineral along with few grains of chalcopyrite and galena.

Pitchblende occurring with pyrite is present as fine orbicular cluster separated by thin disconnected rims of pyrite or as garlands around pyrite. The chemical assay of some important constituents in the ore indicates mineral content of 0.048% and the total sulphur as 0.6%. The sulphur values are contributed by the sulphide minerals mainly pyrite. The Bonds work index of the ore sample is 13.6 "kWh/metric" ton.

A. Acid Leaching

Acid leaching has the advantage of being more effective with difficult ores, requiring lower temperatures and leaching times compared to alkaline solutions. It also requires less pretreatment than alkaline leaching, most notably because the particle size from the grinding process does not need to be as small. Acid leaching is sometimes also referred to as heap leaching because the leaching process can be performed on large "heaps" of metal ore that have been collected from mines. The chemistry of the leaching process revolves around oxidation of the metal compounds, which is typically achieved using manganese dioxide (MnO_2), sodium chlorate (NaClO_3), and Fe (II) salts.

Sulfuric acid is typically used due to the solubility of uranyl sulfate complexes. The reaction is typically performed at slightly elevated temperatures (60°C) and can often release H₂, H₂S, and CO₂ gases during the process. The metal, which typically begins in the tetravalent state, goes through a series of reactions, eventually leading to the formation of the desired complex, [UO₂(SO₄)₃]⁴⁻. While the solubility of this complex makes sulfuric acid a desirable leaching agent, nitric and hydrochloric acid can also be used, but are typically not due to their higher cost and corrosiveness.

B. Alkaline Leaching

While both acidic and alkaline leaching agents are used, alkaline leaching has some significant advantages. Alkaline solutions tend to be more selective to metal minerals, which mean the solution will contain fewer impurities. Consequently, the metal oxide can be directly precipitated without purification. Furthermore, the solutions are less corrosive and can be recycled without the annoyance of increasing impurity concentrations. The alkaline leaching process relies on the formation of highly soluble metaltricarbonate, M (CO₃)₃⁴⁻. As in the case of acid leaching, oxidizers are used to maintain the presence of the hexavalent cation. This can be achieved by simply introducing oxygen into the solution by bubbling air into the solution. The leaching agents used are sodium bicarbonate and sodium carbonate. This prevents formation of metallic hydroxide compounds. Due to the slower reactivity of the alkaline solutions, increased pressures and temperatures are sometimes used to accelerate the process.

C. Reasons for choosing alkaline leaching

There are two operating conditions determined by the geology and groundwater. If there is significant calcium in the ore body (as limestone or gypsum), alkaline (carbonate) leaching must be used. Otherwise, acid (sulphate) leaching is generally better.

Alkaline leaching is effective when compared with acid leaching in cases of high carbonate ores. Alkaline leaching requires the use of a strong oxidant and long retention time to oxidize the ferrous minerals. The chemical nature of the ore determines the type of leach circuit and, in turn, the extent of grinding required. Ores containing greater than 12% limestone require finer grinding (75 µm) and are leached with an alkaline solution.

“Deciding whether to go acid or alkaline and the efficiency of carbonate removal are two critical steps in the process selection and this decision is influenced by the following

1. The size of the resource, grade and number of domains
2. Type and nature of minerals present
3. Mineralogy of the host rock
4. Beneficiation options
5. Impurities in the pregnant liquor or by product opportunity.
- 6.

D. Leaching stoichiometry:

At first U^{IV} will convert to U^{VI}. The alkaline leaching process for metal is well known; it is in fact quite selective towards

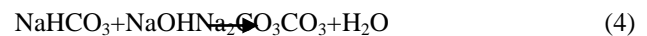
solubilisation of metal values and yield relatively pure leach liquor as compared to acid leaching. The essential chemical reactions in the alkaline leaching of metal ores include oxidation of U^{IV} to U^{VI}.



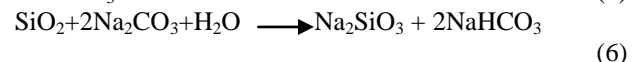
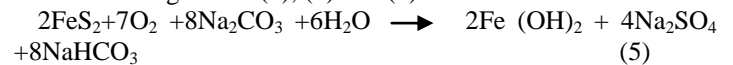
and subsequent dissolution of U^{VI}



The sodium hydroxide generated in reaction (2) could result in precipitation of dissolved metal as per chemical equation (3) and this back precipitation during leaching is prevented by the buffering action of sodium bicarbonate as shown in equation (4).



Depending upon the reaction conditions other minerals present in the ore like sulphides, silica and Alumina too undergo dissolution as given in (5), (6) and (7).



Though sodium carbonate is consumed in different competitive reactions as illustrated in (5), (6) and (7), the consumption is maximum due to sulphide minerals which are more reactive at higher than boiling temperature of water in the presence of oxygen or oxidant. However, the sodium bicarbonate generated as a reaction product can be re-converted to sodium carbonate and re-used or recycled. Similarly sodium sulphate formed during the reaction of sulphides with sodium carbonate has to be taken-out of the process stream as excess concentration would hamper the leaching of concentration would hamper the leaching of metal. The dissolved metal values are precipitated back using the chemical reaction given in equation (3) as sodium diuranate product (SDU).

E. Factors affecting alkaline leaching rate:

Oxidation: Under carbonate leaching conditions, effective oxidation of tetravalent metal can be achieved by molecular oxygen. The rate of oxidation is proportional to the square root of the oxygen partial pressure and can be increased, therefore, by operating with oxygen-enriched air or under high total pressure conditions.

Although more rapid oxidation and improved recoveries can be achieved under alkaline conditions with chemical oxidants (e.g., potassium permanganate) or with air in the presence of an oxidation catalyst (e.g., cupric-ammonia complex), economic conditions generally favor the use of air or oxygen, with relatively long leaching times.

Temperature: Elevated temperatures are necessary to achieve acceptable reaction rates which almost double for each ten-degree rise in temperature between 60°C and 100°C. It must be noted that oxygen solubility (i.e., partial pressure) falls with

increasing temperature under constant pressure conditions and, therefore, a combination of elevated temperature and high pressure gives the highest dissolution rate. Temperatures over 70⁰ C must be used to achieve, acceptable air oxidation rates for tetravalent metal minerals.

Reagent Concentration: Leach solutions contain a mixture of sodium carbonate and bicarbonate, each of which dissolves metal. The rate of dissolution increases with increasing reagent concentration. Some bicarbonate is necessary to prevent re-precipitation of dissolved metal, but excess bicarbonate consumes caustic soda in the precipitation stage. The carbonate concentration is dictated by economic considerations such as soluble losses. Normal concentrations (in circuit feed) are 30 - 60 g/liter Na Co and 5 - 15 g/liter NaHCO₃.

II. EXPERIMENTAL WORK

A. GRINDING:

At first we should grind the run of mine ore with rod mill. Here we are doing wetgrinding because it can eliminate dust problem. We have to grind the material until the product should pass through 200 mesh size sieve (0.074mm). Once the material passthrough 200 mesh sieve we have to collect the slurry. We need to dry the slurry by using tray drier. Once it is dried we can proceed for leaching.

B. FIRST STAGE OF LEACHING

In alkaline leaching 200g of specific grade of Indian ore along with sodium carbonate & bicarbonates of 16g each was taken for the experiment. We add these samples to the 320ml of water in a beaker. Air flow rate of approximately 0.91 lpm maintained by using air compressor. We have to keep this beaker in a heating mantle. Then switch on the heating mantle and set the Temperature to 70⁰c as

a reference. We should give proper agitation to the sample by using stirrer. Whenever temperature reaches 70⁰c we need to run the experiment for six hours. In the entire process we should approximately maintain 70⁰c. To measure the temperature frequently here normal thermometer was used as a temperature measuring device. We can maintain the constant suspension level by adding make up water to the slurry. Temperature exceeds more than 70⁰c because of pyrite reaction. It is an exothermic reaction. After 6 hours we can stop the aeration, stirring and heating. By using vacuum filtration filter the slurry in a counter current manner. In a Buchner funnel we have to properly place the filter paper otherwise solids will appear in final filtered liquid. Vacuum can generate by using vacuum pump. We pour the slurry on top of the filter paper which is placed in Buchner funnel. Because of pressure difference solid-liquid separation will occur. After the separation is over we will wash the residue by taking 70ml of distilled mineral water corresponding to this sodium carbonate & bicarbonate should add to the water. Collect the liquid solution and measure the volume obtained. Again take same amount of water and solvents continue the same procedure to the residue. Note down the volumes obtained in each case, this will help in calculations.

C. SECOND STAGE OF LEACHING:

In second stage of leaching we should take same residue as a feed and add 16g of EDTA to the 320 ml of water. Set temperature to 70⁰c by using heating mantle. We need to run the experiment for 3 hrs with proper agitation. After 3 hrs stop the experiment and do the vacuum filtration. We have to wash the residue with 70ml of water and collect the liquor. All these procedure is mentioned in the above process flow sheet.

D. MATERIALS USED FOR EXPERIMENTAL WORK:

Run of mine ore, Sodium carbonate, Sodium bicarbonate, EDTA, Distilled mineral water, Hydrogen peroxide, NaOH, HCl.

E. EQUIPMENT'S USED FOR EXPERIMENTAL WORK:

Equipment's used for the experiments were Rod mill, Laboratory leaching setup, Heating mantle, Weight balance, UV spectrophotometer, Water bath, Vacuum filter, Air compressor, Tray drier, Quartz crucible.

Four sets of experiments were carried out with above mentioned procedure and the conditions maintained for 179 ppm, 250 ppm, 414 ppm, and 392 ppm are shown in the following Table 1 and 2.

Table 1: Operating conditions for leaching with sodium carbonate and bicarbonate:

Pulp density	50% w/v
Temp	70 ⁰ c
Residence time	6hrs
Na ₂ CO ₃	5%
NaHCO ₃	5%
Aeration	0.91 lpm
Atmospheric pressure	

Table 2: Operating conditions for leaching with EDTA

Pulp density	50% w/v
Temp	70 ⁰ c
Residence time	3hrs
EDTA	5% w/v
Aeration	0.91 lpm
Atmospheric pressure	

In this study I have done the laboratory analysis for uranium and sulphur. Uranium content is measured in the sample by using spectrophotometer. Experimental processes like grinding, leaching and solid-liquid separation is shown in the below figure

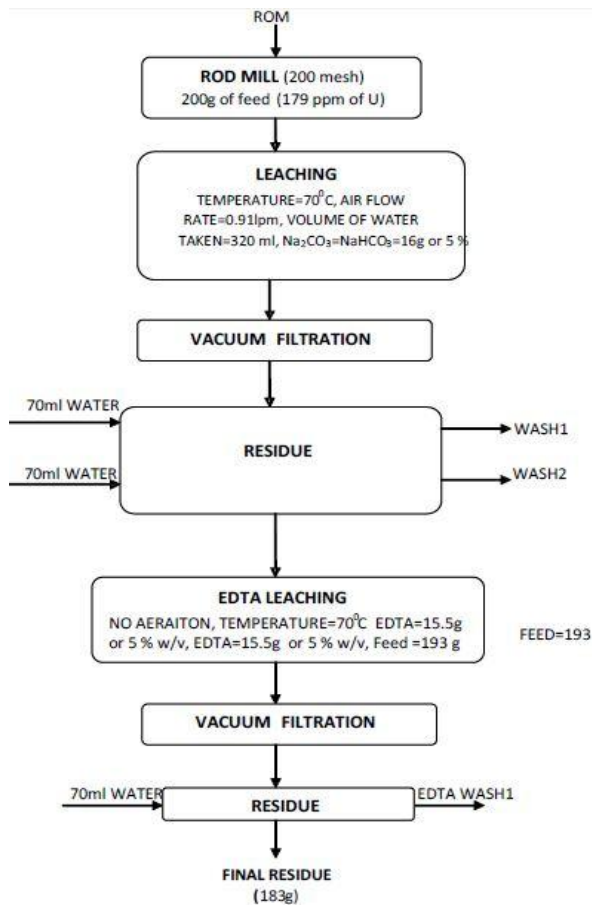


Fig 1: Flow sheet for the two stage leaching

III. RESULTS & DISCUSSIONS:

Four samples A, B, C and D were analysed for radioactive element and sulphur for the solid samples. Liquid samples also were analysed for the radioactive element and sulphate to know the trend of each stage of operations. Results are evaluated equivalent to U_3O_8 representing radioactive element.

Sample D ore:

Metal analysis: Table 3 indicates values of metal analysis for this grade. Table 3 indicates liquid analysis of sample D.

Table 3: Metal analysis for Sample D metal ore

No	Code	ore in gms	U_3O_8 in the sample in mg	% leaching
1	Feed/F3	200	92.454	
2	Residue/F3	187.5	38.812	58.02

From the above metal analysis data table 3 we obtained the percentage of leaching based on alkaline leach liquor is 58%. The percentage of leaching based on feed and residue is 58%. By using EDTA we could leach metal of 2.84% percentage only

calculated based on the liquid sample analysis. So EDTA can't recover metal as we desired i.e. 22-25%.

In the experiment we could not maintain proper aeration due to blockage of air holes with solid particles. In the entire experiment we haven't maintained constant temperature because of inside heat generation due to pyrite (FeS_2) reaction. If we maintain proper aeration and constant temperature we may recover more metal from the Indian ore.

Figures 2 and 3 represent the cumulative recovery of the radioactive element and Sulphur for four samples. Recovery of the metal and Sulphur is proportional proving that the pyrite dissociation releases the radioactive element.

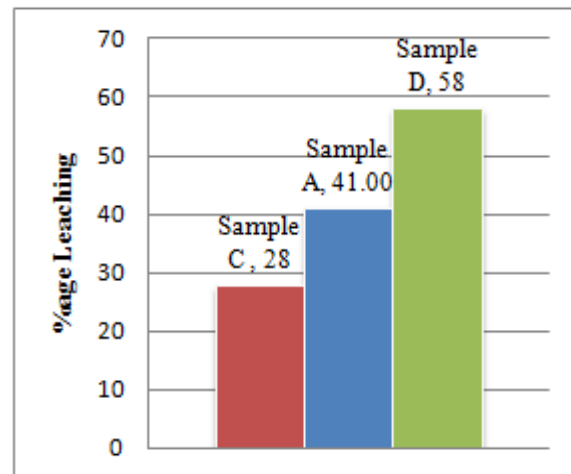


Fig 2: Percentage leaching of radioactive element for three samples

From the above figure 2 more metal could recover with alkaline leaching by using chemicals sodium carbonate and sodium bicarbonate when compared with EDTA leaching.

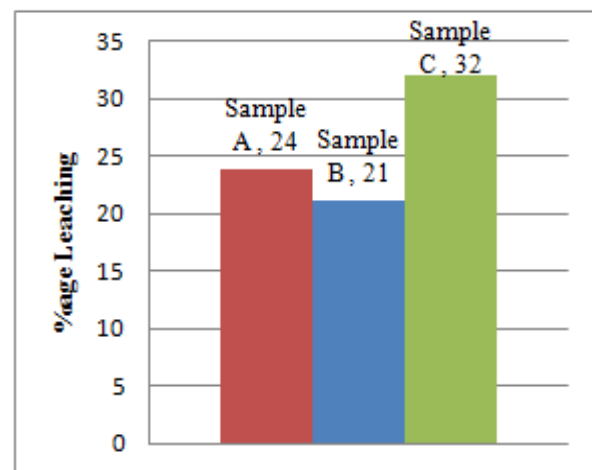


Fig 3: Percentage leaching of Sulphur in the samples

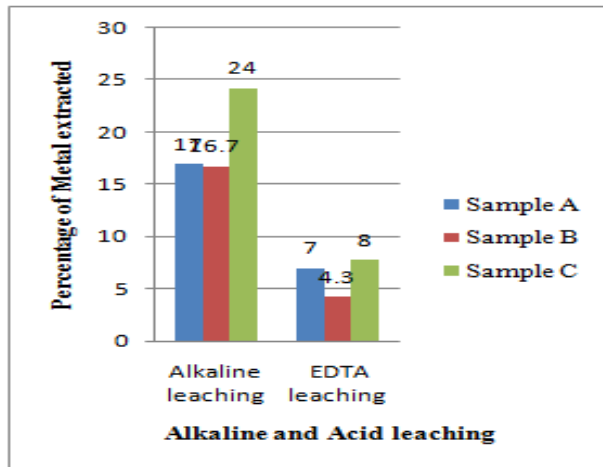


Fig 4: Percentage of metal recovered in alkaline leaching and EDTA leaching

While doing EDTA leaching with aeration we recovered very less percentage of metal content i.e. 2.84% only which is very less when compared with Sample A and B and Sample A ores EDTA leaching without aeration.

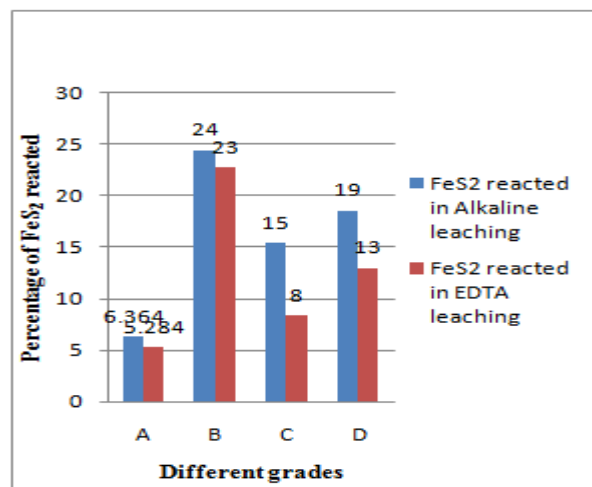


Fig 5: Percentage of FeS₂ reacted in alkaline leaching and EDTA leaching

From the above figure 5 for Sample A ore we are getting 11.64% of FeS₂ reacted from the overall leaching i.e. alkaline leaching and EDTA leaching which is matching with standard data from the books. For the remaining grades of ores we are getting more amount of FeS₂ reacted in leaching which means more error is there while doing laboratory analysis.

CONCLUSIONS

The main points from the present study can be concluded as follows:

1. By doing two stage alkaline leaching we can recover metal up to about 58% by using lixivants sodium carbonate and bicarbonate.
2. Leaching the residue with EDTA solution is not effective. It is not able to recover metal efficiently.

3. Leaching with EDTA can recover metal not more than 10-12%.

4. Recovery of high metal content was better in leaching with EDTA solutions without aeration when compared with EDTA solution leaching with aeration.

5. Because of natural feed contains 83.2% of the carbonate content so alkaline leaching is most preferable with lixivants sodium carbonate and bicarbonate when compared with acid leaching with lixivants sulphuric acid.

6. More metal can be recovered at materials that pass through 200 mesh size (0.074mm) sieve.

7. In this project we haven't done regeneration and recycle of cost intensive reagents but if we do regeneration and recycle we can reduce the fresh reagent inventory to bare minimum level in spite of the need to maintain very high solution concentration of leachants during leaching stage and minimum fresh water inventory.

Acknowledgment

I express my deep sense of gratitude to Shri J.MADHU BABU Scientific Officer, Mineral processing division, Bhabha Atomic Research Centre (BARC), Hyderabad, for his suggestions during experimentation.

My sincere thanks are due to Shri. K. ANAND RAO, Scientific Officer (H), Mineral Processing Division, Bhabha Atomic Research Centre (BARC), Shri.K.C.RAJAN Scientific Officer (H), Mineral Processing Division, Bhabha Atomic Research Centre (BARC), all other technical and non-technical members of the division for their valuable support and encouragement throughout the experimentation.

REFERENCES

- i. A.K. Suri, *Innovative process flow sheet for the recovery of Metal from Tummalapalleore*, issue no. 317, Nov-Dec, 2010.
- ii. A.K. Suri, T. Sreenivas, K. Anand Rao, K.C. Rajan, K. Arinivas, A.K. Singh, K.T. Singh, K.T. Shenoy, T. Mishra, N.P.H. Padmanabhan and S.K. Ghosh, *Process development studies for the recovery of Metal and sodium sulphate from a low grade dolostone hosted stratabound type metal ore deposit*, Vol 123, No 2, 2014.
- iii. Anand Raokacham, A.K.suri, *application of a topochemical reaction model to predict leaching behavior of high carbonate uranium ores in alkaline solutions: An experimental case study*: 2013. *Journal of Hydrometallurgy* 141(2014) 67-75.
- iv. Kazem Mirjalili, Mahshid Roshani, *The Resin in pulp method for uranium recovery from leached pulp of low grade uranium ore*: 2006. *Journal of hydrometallurgy* 85 (2007) 103-109.
- v. F.X. McGARVEY, J. UNGAR, *The influence of resin functional group on the ion exchange recovery of Uranium*, April 1981, *Journal of the South African institute of mining and metallurgy*.
- vi. T. Sreenivas, K.C. Rajan, *Studies on the separation of dissolved uranium from alkaline carbonate leaching slurries by resin in pulp process*, 2013, *Journal of separation and Purification Technology* (2013).
- vii. R. Singh, S.K. Sengupta, P.N. Pathak, A. Chattopadhyay and S.C. Maulik, *Flotation studies on processing of a low grade Uranium ore*, international conference on challenges in coal and Mineral Benefication.
- viii. K. Anand Rao and R. Natarajan, *The selective flocculation of uraninite fines*, 2010.
- ix. S. Purushotham, *Alkaline leaching of Uranium metal from the ore using EDTA*, M.Tech thesis, 2016.