



Unconventional Exploration and Extraction of Uranium through (In situ leaching) ISL Technique

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Summary

Extraction of uranium from low grade ores using conventional mining practices is not economically viable. In situ leaching (ISL) process, also known as solution mining or in situ recovery (ISR), unlike conventional mining wherein the uranium-bearing ore is removed as such from its deposit, involves injection of a leaching liquid through wells into the deposit and pumping out the uranium-bearing liquid to the surface from other wells and subsequent recovery of the mineral. Moreover, there is little surface disturbance and no tailings or waste rock is generated.

Based on the observation of Uranium mineralization on SGR logs, samples were selected from Kaikalur Lingala (KG basin), Karjan-Padra (Cambay basin), Son valley and Sagar areas (Vindhyan basin) for this study. 18 core samples were selected from these areas for study. The core samples were digested with the mixture of suprapure HF, HNO₃ and HClO₄ in the ratio of 4:3:3 and then analyzed on ICP-OES. On the basis of highest Uranium concentration obtained, out of 18 given cores, 05 core samples were selected from different basins (viz., 01A, 02, 11, 13 & 14) for optimization of in-situ uranium leaching process. During the development process, four parameters viz., suitable leaching reagent (HCl, HNO₃ and H₂SO₄), concentration of leaching reagent (0.3% - 5.0%), leaching time (8 -48 hours) and solid-liquid ratio were optimized.

The present study has been undertaken to analyze uranium bearing core and optimizing the chemical processes for in-situ Uranium leaching. The work flow and chemicals identified for the extraction of

uranium from uranium rich rocks during the course of study will help in further extraction efforts.

Introduction

Uranium (U) is a metallic, silver-gray element. It is a naturally occurring element that has the highest atomic weight (~238 g/mole) and is slightly radioactive. It is found in minute quantities in most rocks, soils and waters (normally < 5 ppm), but the real challenge is to find it in high enough concentrations to make it economically viable to mine. Uranium is easily oxidized and forms a number of common uranium oxides and oxy-hydroxide like uraninite (or pitchblende) and schoepite (including meta- and para-). Average Uranium concentration among ores, rocks and water was found highest in black shales which is depicted in Table-1

Table 1: Average uranium concentrations in ores, rocks and waters (ppm - parts per million)	
Material	Concentration (ppm U)
Average granite	4
Average volcanic rock	20 - 200
Average sedimentary rock	2
Average black shale	50 - 250
Average earth's crust	2.8
Seawater	0.003
Groundwater	>0.001 - 8

Uranium is found in soil and water due to the breakdown (weathering) of rocks containing it. Once it is in the soil and water, it may be taken up by plants and consumed by people or grazing

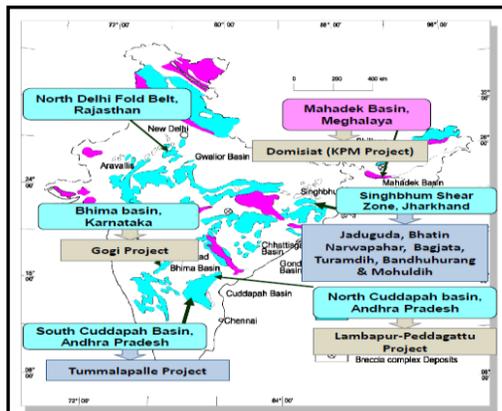
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animals, or it can dissolve in the water to be consumed by any organism.

USSR and USA developed uranium mining technology (In situ leaching) independently in the early 1960s. The method was conceived for extracting uranium from roll-front (infiltration) sandstone type deposits located in water saturated permeable rocks that were not suitable for conventional mining. The recent development is the use of low acid technology in Uzbekistan and the implementation of acid leaching in South Australia.

Uranium ores in India are found both in deep uranium mines as well as in subsurface soil. In India, the Jaduguda Mine is a first uranium mine in Jaduguda village in the Purbi Singhbhum district of the Indian state of Jharkhand. It commenced operation in 1967. The deposits at this mine were discovered in 1951. As of March 2012, India only possesses two functional uranium mines, including this Jaduguda Mine. A new mine, at Tummalapalle in Andhra Pradesh is discovered, recently. The uranium prone areas in India are depicted in Figure 1.

This study aims to recover the maximum uranium



by optimizing the various parameters of in-situ leaching.

Figure1: Uranium industry in growth mode in India

In situ leaching (ISL)

It is also known as solution mining or in situ recovery (ISR) involves leaching the uranium ore in the ground and recovering the uranium by dissolving it from the uranium-bearing minerals by injecting carbonated solution or mild acid and pumping out the leached uranium in a pregnant solution (complex solution of uranium with leaching reagent) to the surface where the metal can be recovered figure 2.

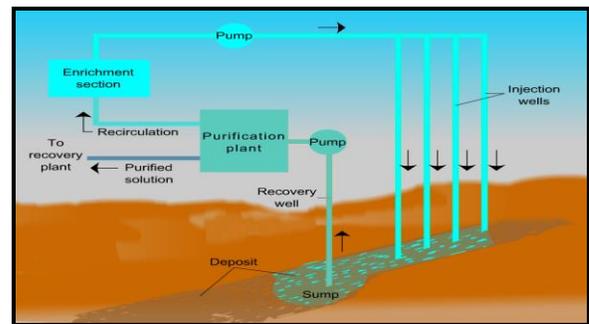


Figure 2: Diagrammatic representation of the ISL technique

In-situ leaching is required where recovery of Uranium from sub-surface Uranium reserves is a major task owing to lower availability, scattered distribution and need for excess lixiviant to extract it from the low grade ores

Chemistry of in situ leaching

In nature, uranium occurs in the tetravalent and hexavalent oxidation states. Tetravalent uranium has a low solubility in both dilute acid and carbonate (alkali) solutions. To achieve economic recovery of uranium in the tetravalent state, oxidation to the hexavalent state is essential.

Tetravalent uranium must be oxidized to the hexavalent form before dissolution occurs in sulphuric acid. Ferric ion (Fe^{3+}) acts as the principal oxidant of tetravalent uranium in acid leaching circuits.

The mechanism for the dissolution of uranium in sulphuric acid is therefore based on the following reactions: The Fe^{3+} oxidizes the tetravalent uranium (U^{4+}) in the solution to the soluble hexavalent uranium (U^{6+}). The Fe^{3+} is then reduced to Fe^{2+} . The oxidant is added to regenerate the Fe^{2+} to Fe^{3+} so that the leach reaction can continue. In

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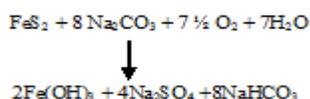
practice it is found that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ is to be considered more important than the uranium reaction. The mechanisms are described by the following reactions with MnO_2 as oxidant.



Alkaline (bicarbonate) leaching is generally used in carbonate rock where acid consumption is high and, as a result, sulphuric acid leaching is unprofitable.

The presence of sulphides, for example pyrite, may result in harmful impurities entering the carbonate leaching solution.

If the sulphide concentration exceeds 2–4%, carbonate leaching becomes unprofitable, and the risk of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation becomes very high. This can cause irreversible plugging of the host rock.



In alkaline environment, oxygen slowly oxidizes tetravalent uranium. Hydrogen peroxide easily decomposes and releases oxygen, which oxidizes tetravalent uranium to the hexavalent state. The dissolved oxygen concentration in the injection fluid is limited by its solubility, and hence, by the available hydrostatic pressure on the host rock. As a result, the carbonate leaching can benefit from using hydrogen peroxide (H_2O_2) as a means to increase the concentration of oxygen delivered to the ore deposit. However, the high cost of H_2O_2 may make its use uneconomic.

Sample details

The presence of Uranium in drilled wells has also been observed on electro logs. On that basis, for Uranium analysis, two core samples from KG basin, two samples from Cambay basin and fourteen samples from Vindhyan basin were selected.

Methodology

The samples were crushed to fine powder (particle size ~25 μm) manually in an agate mortar and pestle. Homogenized powdered samples were weighed (~0.15g) into Teflon beakers and digested with 10 ml mixture of suprapure HF, HNO_3 and HClO_4 (in the ratio of 4:3:3 by volume) on a hot plate and evaporated to dryness. To the dried residue, 1 ml of suprapure HNO_3 and 10-15 ml of triple distilled water was added and the solution was transferred to a 50 ml volumetric flask and made up the volume with triple distilled water. The sample solutions thus obtained were analyzed on an Optima 2000 DV ICP Spectrometer using multi-element standards for calibration. Uranium and two major elements Fe & Ca were determined in each sample.

Criteria for choosing suitable core for ISL Technique

Core samples were acid digested and analyzed on ICP-OES to have a clue (approximate) about the maximum concentration bearing cores. The absolute concentration of U and two major elements Fe & Ca were determined in each sample. The concentration of Fe and Ca is given in Table-2.

Well Name	Fe (%)	Ca (%)	Remark
01A	19.65	0.57	U conc. was high
02 A	20.56	0.57	U conc. was high
26	0.71	0.05	
35	7.44	0.14	
11 A	2.62	0.23	U conc. was high
11 B	2.78	0.03	
14 A	3.46	0.27	U conc. was high
17	2.15	0.18	
14 B	1.70	0.18	
14 C	0.82	0.13	
14 D	2.39	0.23	
22	17.49	0.61	
13A	20.43	0.56	
13 B	0.67	0.56	
13 C	6.93	0.14	
13 D	3.05	0.04	
13 E	2.81	0.04	U conc. was high

Table 2: The concentration of Iron and calcium in the studied samples

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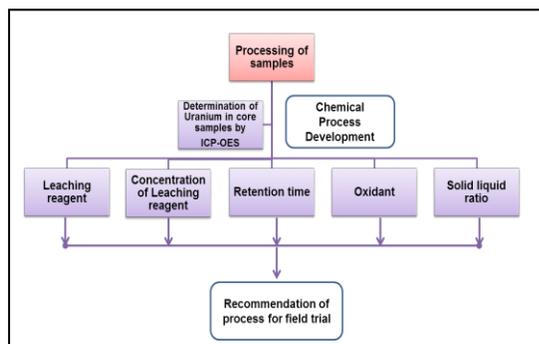


Figure 2: Diagrammatic representation of the criteria for selection of samples and leaching parameters for ISL Technique

For further studies five core samples, 01A, 02A, 11A, 14A and 13E were selected on the basis of their maximum uranium concentration in digested core sample. The type of leaching preferred is selected on the basis of calcium concentration. As in selected samples the concentration of calcium is less than 2%, the preferred mode of leaching remains acidic due to the accelerated kinetics of leaching with the uranium recovery being 80-90%, versus 60-70% for carbonate reactants and a higher uranium concentration in the recovered solution. The concentration of iron in selected samples was more than 1 %, so there is no need of adding any chemical oxidant. Acid leaching has the advantage of being more effective with different ores, requiring lower temperature and less leaching time compared to alkaline leaching.

Results and Discussion

For chemical process development of in situ Uranium leaching, four parameters were optimized:

- Leaching reagent
- Concentration of leaching reagent
- Leaching time
- Solid-Liquid ratio

All the experiments were conducted on 30^oC considering it as ambient temperature of the field.

Leaching reagent and its concentration

Three different acids namely sulphuric, nitric and hydrochloric acids (0.3% concentration of each acid) were used as lixiviant to find out the suitable one on the basis of maximum uranium recovery. In all the five selected samples it was found that out of the three acid used (sulphuric, nitric and hydrochloric acids) in various concentration (0.3 to 2.0%) the recovery was maximum with sulphuric acid. In core samples 01A, 02A and 11A the concentration of sulphuric acid was optimized with 1%. In sample 14A and 13E sulphuric acid concentration was found to be 1.5% and 2.0% respectively.

Leaching time

~1gm of powder sample and 0.3% of H₂SO₄ is used for Uranium recovery at different leaching time (8 hrs. 16 hrs. 24 hrs. and 48 hrs.). In all five selected samples considering all leach duration, the recovery of Uranium in leachate solution was maximum with 24 hrs. except in sample 01A where it was found 16 hrs.

Solid-Liquid ratio

Different solid liquid ratios (1:10, 1:15 and 1:20) were used with 1.0% sulphuric acid to find maximum Uranium recovery. In all the five selected core samples the maximum uranium recovery is found with 1:15 solid-Liquid ratio i.e. 1 gm of solid in 15 ml of leaching agent.

Conclusion

The acidic leaching is more preferable in comparison to alkaline leaching due to low concentration of calcium (<2%). In alkaline leaching the uranium recovery was insignificant. Thus this study is focused only on acidic leaching.

In all the five selected samples it was found that most suitable leaching reagent was sulphuric acid. In core samples 01A, 02A and 11A the concentration of sulphuric acid was optimized with 1%. In sample 14A and 13E sulphuric acid



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