

Innovative process flowsheet for the recovery of Uranium from Tummalapalle Ore

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1. INTRODUCTION

Natural uranium ($\sim 99.3\% \text{U}^{238} + \sim 0.7\% \text{U}^{235}$) is the basic raw material for nuclear fuel in Pressurized Heavy Water Reactors (PHWR). The energy in the reactor is derived from the 'fission' of U^{235} , the only 'fissile' isotope in nature. These reactors also transmute the more abundant U^{238} to man-made fissile isotope Pu^{239} , which could be subjected to multiple recycling, as fuel, in fast reactor for efficient utilization of natural uranium resources and to ensure long term sustainability of nuclear energy. Thus the Indian nuclear power program has accorded a high priority to the use of all the three main fissionable materials, U^{235} , Pu^{239} and U^{233} , to meet the challenge of reaching energy independence through a well calibrated deployment of domestic uranium and thorium resources (Anil Kakodkar, 2008). Though the country has good resource base of thorium which is the precursor of U^{233} , the conventional uranium ore deposits are limited and lean in tenor. The indigenous supply of uranium to the power reactors of the country is met mainly from the uranium ore deposits located in East Singhbhum of Jharkhand mined at Jaduguda and Turamdih. The rising demand for nuclear power has naturally necessitated increased supplies of uranium. In view of this, the Department of Atomic Energy (DAE) has launched an aggressive exploration campaign for augmentation of indigenous uranium ore resources. Simultaneously research activity

aimed at development of environmentally friendly technologies for the exploitation of various types of ore deposits has also been given renewed thrust.

Amongst the potential uranium ore deposits discovered by the Atomic Minerals Directorate for Exploration and Research (AMD), the exploration wing of DAE, out-side the Singhbhum Thrust Belt in Jharkhand, the Proterozoic Cuddapah Basin in southern India emerges as a major uranium province. Sustained exploration by AMD since 1986 had indicated a potential 160 km long belt of carbonate hosted stratabound uranium mineralization in impure dolostone of the Vempalle formation with the establishment of a low-grade but large tonnage uranium deposit in Tummalapalle - Gadankipalle area in Cuddapah district of Andhra Pradesh (Dhana Raju et al, 1993). Detailed exploration carried out over a stretch of about 9.5 km so far in Tummalapalle - Rachakuntapalle tract (Fig. 1) has established a resource of 29000 tonnes of U_3O_8 in about 61 million tonnes ore of 0.05% eU_3O_8 (Rai A.K. et al., 2009). The complex nature of uranium mineralization in the ore viz. absence of discrete mineral phase, ultra-fine dissemination in various minerals, lean tenor and the need for deploying the alkaline leaching route for its extraction warranted exhaustive research investigations for making the process flowsheet techno-economically viable as well as eco-friendly. It may be noted that the existing uranium ore processing mills at Jaduguda and Turamdih in India

use conventional sulfuric acid leaching technology for the production of yellow cake or magnesium diuranate, hence the switch-over to alkaline leaching technology on commercial scale would be a first time venture.

The following discussion presents the salient features of the ore processing flowsheet for uranium recovery from the Tummalapalle ore which was the fore-runner for the commercial plant coming up at Tummalapalle in Andhra Pradesh with a slated capacity to treat 3000 tonnes of ore per day using state-of-art alkaline pressure leach process technology.

The research and development work on the Tummalapalle ore encompassed not only the bench-scale experimental studies in the laboratory but also setting-up of Technology Demonstration Pilot-plant for alkaline processing of uranium ores at M/s UCIL complex, Jaduguda, with combined efforts of Scientists and Engineers of BARC, NPCIL, AMD and UCIL (Suri A.K. 2008 and Suri A.K. *et al.*, 2009).

2. PROCESS DEVELOPMENT

Nature of host rock of valuable mineral/metal determines the process development strategy in any ore processing scheme. It is all the more critical in processing of uranium ores as the purity levels of final product in processing scheme – yellow cake, is very demanding. Achieving of good quality yellow cake product from low-grade uranium ores ($U_3O_8 < 0.2\%$) is quite challenging.

The different process options generally considered for the exploitation of low-grade ores are (i) pre-concentration of the valuable mineral by suitable physical separation technique followed by leaching of the pre-concentrate and (ii) direct “whole ore leaching” technique. Pre-concentration by physical separation methods would result in reducing the mass of the ore that goes for chemical attack subsequently. Thus the “pre-concentration - chemical leaching” route has got obvious technical, economical and environmental advantages. However, the absence of discrete uranium phase in physically recoverable size ranges in the Tummalapalle ore eliminates the application of physical beneficiation for direct pre-concentration of the uranium values. Nevertheless, the technique of “reverse physical beneficiation” for the separation of sulphide minerals as well as “thermal processing” methods like calcination-quenching-dissolution / desliming were attempted. The limited success met with all the pre-concentration methods prompted for

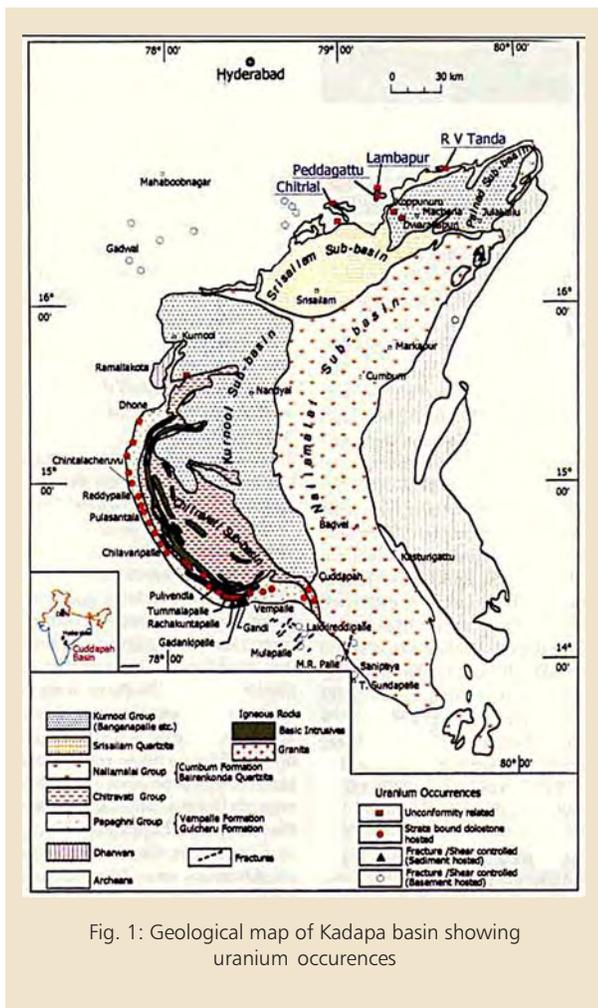


Fig. 1: Geological map of Kadapa basin showing uranium occurrences

choosing direct “whole ore leaching” route for the recovery of uranium values from the Tummalapalle ore.

The generic flowsheet for chemical processing of uranium ores consists of different unit operations like, comminution, leaching, solid-liquid separation, liquor purification, precipitation of dissolved uranium and effluents processing. The type of leaching - acid or alkaline, depends upon the nature of the host rock. Wherever the host rock is acid consuming in nature, alkaline route is chartered upon. Since the host rock for uranium mineralization in Tummalapalle deposit is primarily dolostone type only alkaline leaching route is viable for the recovery of uranium values.

Amongst the various unit operations mentioned earlier for uranium ore processing, the leaching stage is of critical significance as higher the leachability attained higher would be the yield of the final product. Sub-optimal leachability of uranium would have high negative impact as more than 50% of the direct extraction cost is towards mining and comminution. Leaching of uranium values can be accomplished under normal or elevated pressure and temperature conditions. The choice depends upon the nature of mineralization of valuable mineral. Generally refractory mineral phases, either physical or chemical, require drastic leaching conditions which are possible only in an autoclave reactor. Similarly, solid-liquid separation of alkaline leach slurries is rather sluggish due to high viscosity of alkaline solutions. Optimum process conditions have to be developed diligently for increasing the rate of filtration with minimum dissolved solute loss in the leach residue. Though alkaline leaching with sodium carbonate - sodium bicarbonate reagent combination is relatively selective in comparison to sulfuric acid leaching, the process conditions are very aggressive and chemicals or lixivants are very expensive underlining that their inventory too plays vital role in overall economy. Thus the focus of bench

scale studies on Tummalapalle ore was centered on (i) atmospheric as well as autoclave leaching, (ii) filtration of leach slurry, (iii) determine the threshold uranium concentration required for direct precipitation of uranium from the leach liquor efficiently both quality-wise and quantity-wise, (iv) reagents recovery and (v) flowsheet synthesis cum locked-cycle testing.

2.1 Characterisation

The mineralogical composition of the exploratory mine ore sample used for the flowsheet development work (Table 1) 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. The iron

Table 1: Mineralogical Composition of Tummalapalle Uranium Ore

Mineral	% Weight
Carbonates	83.2
Quartz + Feldspar	11.3
Collophane	4.3
Pyrite	0.47
Chalcopyrite	0.05
Galena	Traces
Magnetite	0.15
Ilmenite + Leucoxene	0.25
Iron Hydroxide (Goethite)	0.27
Pitchblende in intimate association with Pyrite	0.1
Total	100.0

bearing oxides are magnetite, ilmenite and goethite. Heavy media separation of various closely sized feed fractions using bromoform (BR) and methylene iodide (MI) liquids have indicated that about 91% of the uranium values are present in lighter fractions (specific gravity <3.2) (Fig. 2) as ultra-fine disseminations. The remaining 9% of uranium values reporting in methylene iodide heavies fraction are accounted towards discrete pitchblende, which is mostly associated with pyrite. 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 U_3O_8 content of 0.048% and the total sulfur as 0.6% (Table 2). The sulfur values are contributed by the sulfide minerals mainly pyrite.

The Bonds Work Index of the ore sample is 13.6 kWh/metric ton.

2.2 Process Chemistry

The alkaline leaching process for uranium is well known; it is in fact quite selective towards solubilization of uranium values and yield relatively pure leach liquor as compared to acid leaching. The essential chemical reactions in the alkaline leaching of uranium 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 uranium 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].

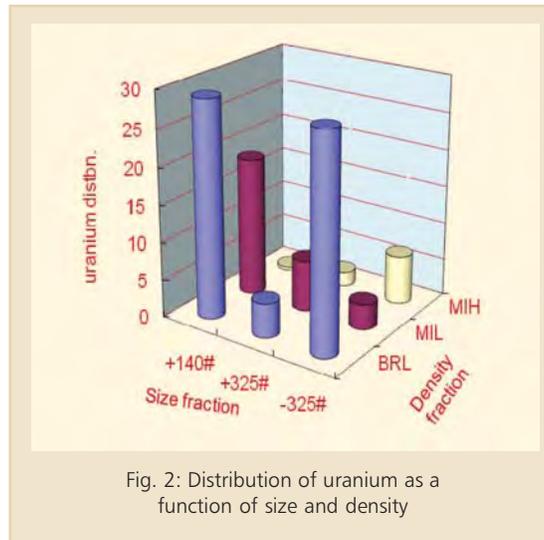
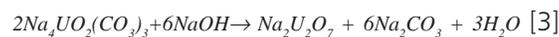
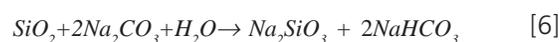
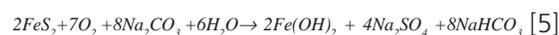


Fig. 2: Distribution of uranium as a function of size and density



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 sulfide 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 sulfate formed during the reaction of sulfides 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 uranium. The dissolved uranium values are precipitated back using the chemical reaction given in [3] as sodium diuranate product (SDU).

2.3 Process Flowsheet

Extensive laboratory studies were carried out on alkaline leaching - both atmospheric and under elevated temperature and pressure, under various process variable settings, which include mesh-of-grind, oxidant, lixiviant dosage, contact time, temperature and pressure. As an illustration the leachability obtained with different oxidants are shown in Fig 3. Based upon the outcome of bench-scale studies, a tentative process flowsheet was developed with alkaline pressure leaching for solubilizing the uranium values from this ore using sodium carbonate as leachant, industrial oxygen as the oxidant at elevated temperature and pressure. The major issue was containing the loss of uranium and the price of uranium to a value comparable to the existing price structure. For this, the process flowsheet was engineered in such a manner that both the objectives could be achieved by alkaline processing scheme. The laboratory experiments were carried out to simulate the tentative scheme and on achieving a positive result a decision was taken

up to set up a pilot-plant facility at the premises of Uranium Corporation of India Limited, Jaduguda and test the process on a pilot-scale. Batch type pilot facility was set up by middle of 2005 and on its successful demonstration it was decided to design and set up a continuous leach autoclave reactor to gain an operating experience as well as generate engineering data for setting up of a commercial plant.

A schematic process flowsheet developed for the recovery of uranium values from the Tummalapalle ore is given in Fig. 4.

Since the uranium content of the ore is very low, 0.05% U_3O_8 , and a minimum concentration of leachant has to be retained for effective leaching of the ore, a leaching circuit with counter-current washing was found to be very effective in reducing the loss of uranium to the tailings. By re-circulating most of the leach liquor, with a small fraction as bleed, the concentration of uranium in the leach liquor could be raised to a level which is suitable for direct precipitation of uranium as sodium diuranate. The distribution of chemical species in the SDU cake of Tummalapalle is shown in Table. The leach liquor after precipitation of uranium contains large proportion of reagents with

substantial concentration of sodium, carbonate, hydroxyl and sulfate ions. While sulfate is recovered as by-product by either freeze crystallization or evaporation. Rest of the solution is suitable as feed for the regeneration of lixivants. Causticization of certain fraction of the solution followed by carbonation has been adopted to reuse almost all the reagents. In this process scheme the solution balance and the solution

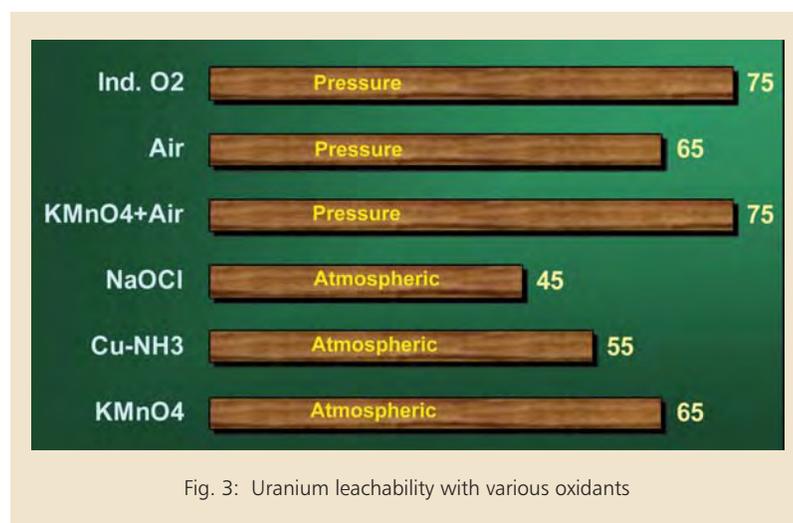
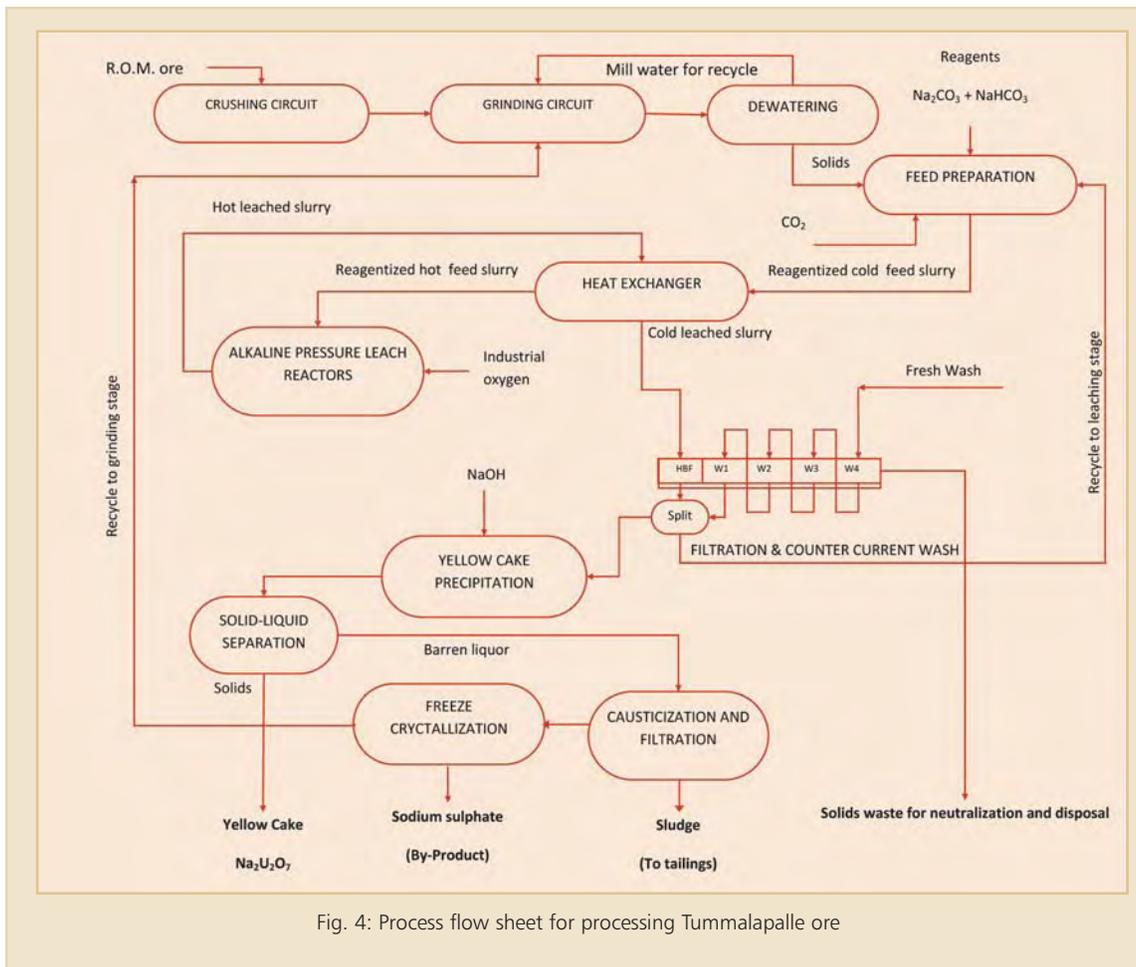


Fig. 3: Uranium leachability with various oxidants



chemistry control is extremely important to attain the twin objectives of reducing the uranium loss and obtaining uranium concentration suitable for direct precipitation. These have been accomplished both in the laboratory and in pilot-plant.

2.4 Interesting Features of the Process

The process flowsheet developed for the Tummalapalle ore could qualify for commercial exploitation mainly due to certain special attributes imbedded in the overall exploitation scheme, which include:

- Fewer number of processing stages as compared to conventional uranium ore processing flowsheet;
- Regeneration and recycle of cost-intensive reagents thereby reducing the fresh reagent inventory to bare minimum level inspite of the need to maintain very high solution concentration of leachants during leaching stage and, minimum fresh water inventory;
- Relatively pure yellow cake product with U_3O_8 assay of about 77 - 80% and with minimum impurities load for subsequent yellow cake processing stage.
- Stabilized tailings for safe disposal to environment and practically zero liquid waste generation.
- A technology which has relatively low equipment corrosion in comparison to conventional sulfuric acid leaching route.

- Production of sodium sulfate by-product with less than permissible levels of radioactivity.

Thus many challenges inherent in the ore characteristics were converted into opportunities such that a vast resource could be put to use for Country's nuclear power programme at a competitive cost.

3.0 CONCLUSIONS

A good understanding of the nature of mineralization of uranium values in the ore, uranium process chemistry and different unit operations, has led to the development of well integrated specially engineered alkaline leaching process flowsheet to treat the low-grade uranium deposit in the alkaline host rock. The objective of making a techno-economically viable process flowsheet could be realized primarily by reducing the number of stages of unit operations and conservation of leachants by regeneration and recycle. Effective recycle of process solution led to minimization of fresh water inventory as well as quantum of liquid effluent discharge. Inevitable chemical species viz. sodium sulphate and calcium carbonate, in the process were converted into useful by-products by carefully tailored sequence of chemical steps. The process technology developed is being translated for industrial adoption by UCIL and the mine and the mill are in advanced stages of completion.

4.0. REFERENCES

Anil Kakodkar, 2008. *Evolving Indian Nuclear Power Programme: Rationale and Perspective*. Nuclear India, Volume 41, No. 11-12, May - June 2008.

Dhana Raju, R, Minati Roy, Madhuparna Roy and Vasudeva, S.G. *Uranium Mineralization in South-western part of Cuddapah Basin: A Petromineralogical and Geochemical Study*, Journal of Geological Society of India, Vol. 42, Aug 1993, pp.135 - 149.

Rai A.K., Zakaulla S., Chaki Anjan, 2009. 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: Exploration, Mining, Production, Supply and Demand, Economics and Environmental Issues (URAM-2009) 22-26 June 2009, Vienna, Austria.

Suri, A.K., 2008. Uranium Processing – A New Alkaline Route. Transaction of Indian Institution of Metals, Vol.61, No.1., February 2008.

Suri, A.K., Ghosh S.K. and Padmanabhan N.P.H. Recent Pilot-plant Experience On Alkaline Leaching of Low Grade Uranium Ore In India. Presented at International Symposium on Uranium Raw Material for Nuclear Fuel Cycle (URAM 2009) organized by IAEA, Vienna, Austria, June 22-26., 2009. Paper IAEA-CN-175/65

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