Autoclave Leaching of Refractory Uranium Minerals

Mineral Processing Division

Abstract

Autoclave circuits have been proven as reliable unit operations in hydrometallurgy, for treating refractory ores - either physical or chemical type. They yield high leach efficiency and produce stabilized leach residues, which are environmentally least harmful. Sustained R & D efforts in BARC have resulted in successful use of autoclave reactors, for the dissolution of refractory uranium minerals (viz. davide, betafite, liandratite) and ores with extremely fine dissemination of uranium phases. This paper gives an overview of the studies.

Keywords: Uranium, Leaching, Autoclave, Pressure, Mineral processing.

Introduction

There are approximately 205 species of uranium minerals, occurring in 14 types of uranium deposits [1,2]. Uranium minerals can be grouped into various chemical categories such as oxides (uraninite, pitchblende), hydrated oxides (becquerelite, gummite), Nb-Ta-Ti complex oxides (brannerite, davidite), silicates (coffinite, uranophane, uranothorite), phosphates (autunite, torbernite), vanadates (carnotite, tyuyamunite) and hydrocarbons (thucholite, asphaltite). Simple oxide minerals like uraninite and pitchblende are relatively easily leachable, while the rest of them are not so leachable. Depending upon the ease of dissolution / leachability, the uranium minerals are categorized as (a) slightly refractory (oxidation is required prior to leaching e.g. coffinite & uranothorite), (b) moderately refractory (requires higher leach temperatures, greater free acid and oxidant concentration and longer leach periods e.g. brannerite, thucholite & davidite); and (c) highly refractory (requires extreme leach conditions e.g. betafite & pyrochlore). In addition to the chemical refractory nature of some of the uranium minerals, there exists certain uranium ores which inspire of having simple uranium oxide phases, yield low leach recovery due to the physical nature of occurrence of uranium in them. To this category, belong ores having uranium mineralization in very-fine to ultra-fine sizes, either in discrete form and/or as disseminations in various gangue minerals. These ores too demand rigorous leaching conditions for quantitative dissolution, which could be elevated temperature and pressure, finer grind, higher oxidation potential, higher leachant dosage, longer contact time etc.

Autoclave circuits have been proven as reliable unit processes, in maximizing the leachability of valuable minerals, which are not only chemically refractory in nature but also those ores which have the required minerals, in physically refractory form. Besides increasing the leach efficiencies and kinetics, the autoclave reactors also give
stabilized leach residues, which can be safely disposed [3]. The use of autoclaves in uranium industry was in vogue since early 1950’s [4,5]. Table 1 gives details of some prominent uranium mills using this technology. In the earlier days pressure leach technology was justified for only high grade uranium ores, due to its cost-intensive nature. However, increasing demand for uranium, upward trend in uranium metal price and growing environmental awareness, triggered the use of pressure leaching technology, even for low and medium grade uranium ore deposits. The technology is also being adopted by installations processing uranium bearing mine dumps or waste [6]. Uranium ore processing mills use either Pressure OXidizing autoclaves (POX) or HIgh Pressure Acid leach autoclave technology (HiPAL) depending upon the mineralogical characteristics of the ore, type of leaching followed – acid or alkaline, and on the type of oxidant as well as the level of oxidizing environment, necessary during the leaching reaction [4,5]. Similarly different types of autoclaves – vertical or cigar type/ horizontal or in some cases, pipe autoclave reactors were investigated, for their suitability in uranium leaching application [4,7]. This paper discusses the recent R & D and pilot-plant scale studies, carried out in our Division, on the utility of autoclave reactors in processing various refractory uranium ores. An outcome of these studies is the establishment of India’s first uranium mill with alkaline pressure leach technology at Tummalapalle in Andhra Pradesh.

### Leaching Chemistry of Uranium Minerals

The common oxidation states of uranium, in its minerals like uraninite, pitchblende, coffinite and numerous others, are +4 and +6. Amongst the two oxidation states, U\(^{+6}\) is soluble in aqueous media under suitable E\(_{H}\) – pH conditions, while U\(^{+4}\) is practically insoluble. The uranium minerals occurring in various ore deposits consist predominantly of uranous ion (U\(^{+4}\)), necessitating the use of an oxidant and other lixivants, for quantitative dissolution during leaching. The type of leaching - acid or alkaline mode depends upon the host rock. Sulfuric acid is the common leachant in acid leaching process, while Na\(_2\)CO\(_3\) - NaHCO\(_3\), (NH\(_4\))\(_2\)CO\(_3\) and NH\(_4\)HCO\(_3\) are the widely used lixivants in alkaline leaching of uranium ores. The oxidant reagents could be either chemical or gaseous in nature. A typical chemical reaction in alkaline leaching of UO\(_2\) with carbonate ions and oxidant (X) is given in Equation 1, a similar equation can be written for the sulfuric acid leaching process.

$$\text{UO}_2 + 3\text{CO}_3^{2-} + X \rightarrow \text{[UO}_2\text{(CO}_3\text{)}_{3}]^{4+} + \text{X}^2. \quad (1)$$

### Table 1: Uranium plants with acid or alkaline pressure leach technology [4, 5].

<table>
<thead>
<tr>
<th>Plant Details and Year of commencement</th>
<th>Type of leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eldorado Nuclear Ltd., Beaverlodge Mill, Uranium City, 1953</td>
<td>Alkaline</td>
</tr>
<tr>
<td>SaskatchewanAtlas Corp., Minerals Division, Moab Utah, 1956</td>
<td>Alkaline</td>
</tr>
<tr>
<td>United Nuclear-Homestake, Partners, Grants New Mexico, 1958</td>
<td>Acid</td>
</tr>
<tr>
<td>Cotter Corporation, 1970</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Canon City Colorado, 1980</td>
<td>Acid</td>
</tr>
<tr>
<td>Lodeva Mill, France, 1980</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Rio Algom Corp., Lisbon Mill, Moab Utah, 1980</td>
<td>Alkaline</td>
</tr>
<tr>
<td>Key Lake Mining Corp., Key Lake, Saskatchewan, 1972</td>
<td>Acid</td>
</tr>
<tr>
<td>COGEMA Resources Inc., McClean Lake, Saskatchewan, 1983</td>
<td>Acid</td>
</tr>
<tr>
<td>Uranium One Inc. Dominion Reefs Mill, S Africa, 2008</td>
<td>Acid</td>
</tr>
</tbody>
</table>
Case Studies

**Oxidative pressure leaching of uranium from a dolomitic limestone ore**

India has a medium-tonnage, low-grade uranium ore deposit of siliceous dolomitic phosphatic limestone type, in Kadapa district of Andhra Pradesh. Detailed exploration carried out in a stretch of about 9 km in this area, established a resource of 29000 t of \( \text{U}_3\text{O}_8 \) with a cut-off grade of 0.025% \( \text{U}_3\text{O}_8 \) [8]. Mineralogical studies on an exploratory mine ore sample from this area, indicated the occurrence of uranium values predominantly as ultra-fine dissemination, in lighter gangue minerals (specific gravity less than 3.2). It also occurs, albeit to a minor extent, in the form of ultra-fine pitchblende in association with pyrite, as disseminations in collophane-rich parts, coffinite and as U-Ti complex. Carbonate minerals constitute the major gangue present in the form of dolostone (~80%). 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 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 minerals (specific gravity <3.2) (Fig. 1), as ultra-fine disseminations. The remaining 9% of uranium values reported in methylene iodide heavy fraction, are accounted by discrete pitchblende, which is mostly associated with pyrite and collophane. Pitchblende occurring with pyrite is present as fine orbicular cluster, separated by thin disconnected rims of pyrite or as garlands around pyrite.

Atmospheric alkaline leaching studies, carried out on this ore sample, by varying important process parameters like mesh-of-grind, temperature, contact time, dosages of leachants - sodium carbonate and sodium bicarbonate, solids concentration and type of oxidant, gave a maximum \( \text{U}_3\text{O}_8 \) leachability of 65% (Fig. 2). Studies with other oxidants like NaOCl, Cu-NH\(_3\), oxygen and air gave poor leachability in comparison to KMnO\(_4\), emphasizing the need for strong oxidizing conditions during the dissolution process. However, as KMnO\(_4\) cannot be used as an oxidant on commercial scale due to its expensive nature, the only alternative is to carryout the leaching reaction in a pressure reactor, using a gaseous oxidant. Since the solubility of oxygen diminishes with increasing temperature, adoption of higher partial pressure aids in increased dissolved oxygen concentration. Detailed analysis of the leach residue obtained in the atmospheric leaching experiments indicated, that uranium values associated with pyrite are not completely leached at temperatures <100\(^\circ\)C. Further, some of the locked-up uranium values in various gangue

![Fig. 1: Distribution of mass and uranium values of a dolomitic limestone ore, Kadapa district (A.P.) in various heavy media fractions](image)

![Fig. 2: Atmospheric leaching of uranium from dolomitic limestone type ore of Kadapa district (A.P.). Mesh of grind - 100#, Sodium carbonate 50 kg/t, Sodium bicarbonate 50 kg/t, KMnO\(_4\)10 kg/t,](image)
phases, require more aggressive diffusion conditions for penetration of the leachant to the desired mineral interface. Both these requirements can be realized only at elevated temperature and under sustained oxidizing conditions, possible in an autoclave reactor. Leaching at elevated temperature and pressure was initially carried out in a laboratory, 5 liter S.S. autoclave reactor equipped with necessary instrumentation and control to maintain preset temperature, overpressure and agitation speed of the impeller. All the autoclave leaching experiments were carried out, at optimum dosage combination of sodium carbonate and sodium bicarbonate evolved in atmospheric leaching, that is - 50 kg/ton and - 70 kg/ton respectively. The autoclave leaching studies mainly addressed the dissolution of uranium associated with pyrite and the scope of replacing KMnO₄ with industrial oxygen. Figs. 3 and 4, illustrate the effect of temperature and contact time on the leachability of uranium values, observed under aggressive conditions. About 75% of uranium values were leached at a reaction temperature of 125 - 130°C in 3 h of contact time, using a feed ground to 65% weight finer than 200#. Increasing the fineness of grind in -200# to 85% showed, an enhancement in leachability to about 80%. Based on these results, large-scale leaching studies were carried out, both on batch and continuous leach reactor, to generate necessary scale-up and engineering data for industrial scale reactor, besides verifying the reproducibility of results at higher-scale of operation. Both the batch and cigar type continuous reactor were of 850 liter capacity with inconel 600 as material of construction. The kinetic profile of the leaching reaction in pilot scale batch and continuous reactor is illustrated in Fig. 5. Large-scale studies confirmed the results generated in batch scale experiments. At present, DAE is setting-up a 3000 tpd capacity uranium mill at site, wherein two 720 m³ capacity autoclave reactors with inconel 600 cladding for the wetted parts will be used. This will be the first uranium plant, using autoclave leaching technology in India.

**High acid pressure leaching of uraniferous alkali syenite ore containing betafile**

Uraniferous alkali-syenite ore deposit in Vellore district of Tamilnadu, analysing 0.04% U₃O₈ containing betafile -(Ca,U)₂(Ti,Nb,Ta)₂O₈(OH) as the main radioactive mineral, was studied for recovering uranium values. The other radioactive minerals in the ore include pyrochlore, uranathorite, thorite, cyrtolite, monazite and minor...
concentrations of some secondary uranium minerals. Practically all the uranium-bearing phases are refractory in nature. The main gangue minerals in the ore are feldspar (83%), pyriboles (3.3%), iron oxides (2.9%), sulfides (0.1%), limonite (1.6%), barite (0.9%) etc. Since the major gangue of the ore is non-acid consuming in nature, the ore was processed by the sulfuric acid leaching route. Various process options were tried to extract the uranium values, which included physical beneficiation followed by acid leaching of the pre-concentrate, pug-cure-leaching, direct acid leaching of the ground ore at atmospheric pressure and normal temperature conditions and finally sulfuric acid leaching under aggressive temperature and pressure. Atmospheric leaching experiments indicated the scope of leaching to about 80% of the uranium values with high sulfuric acid dosage, about 200 kg/ton, at about 90°C. Though the leachability is reasonably satisfactory, the high residual SO$_4^{2-}$ / HSO$_4^-$ in the leach liquor, limits the efficiency of down-stream unit operations, particularly ion-exchange, tailings neutralization etc. Studies carried out at elevated temperature in an autoclave reactor, have indeed yielded twin benefits of reducing the acid consumption to 90 kg/ton and enhancing the leachability to 88-90% at about 150°C (Fig. 6) in 8 h contact time (Fig. 7). XRD analysis of feed and various leach residues have indicated, that the leachability of other-wise refractory uranium mineral phases could be accomplished within commercially acceptable operating conditions, due to the presence of both betafite and thorite in metamic form. Encouraging results obtained in the autoclave reactor generated significant interest in the exploration geologists, working on this potential deposit.

**High acid pressure leaching of uranium from liandratite**

High sulfuric acid pressure leaching was also found successful in leaching uranium values from liandratite, a uranium bearing niobium-tantalum oxide refractory mineral, with the chemical formula [U(Nb, Ta)$_2$O$_8$]. As the chemical reactivities of uranium and Nb & Ta are different, a separate sequence of chemical conditions is required for maximal dissolution of individual metals. Leaching of niobium and tantalum oxides required, highly acidic or highly alkaline aqueous conditions, for quantitative dissolution at very high temperature. Unlike niobium and tantalum, the acidity or alkalinity necessary for uranium leaching is significantly lower. In view of this, the scheme for extracting the metal values from a liandratite bearing ore sample (Table 2), is formulated in such a way, that in the first stage, conditions were set to leach as much uranium values as possible, followed by re-adjustment of the chemical and experimental conditions, for dissolution of niobium and tantalum values. Optimal process conditions gave uranium leachability of about 80% at a reaction temperature of 180°C, sulfuric acid dosage...
of 400 kg/ton, feed ground to finer than 150 \( \mu \)m and contact time of 48 h. There was no necessity of adding any additional oxidant during the leaching reaction, as sulfuric acid itself served as a strong oxidizing agent, due to its high concentration. The redox potential was consistently about 450–500 mv (vs. SCE). The solution composition of the leach liquor indicated the presence of niobium and tantalum concentration of 5 mg/l and 30 mg/l against uranium concentration of 21 g/l, indicating that the leaching conditions are good for selective dissolution of uranium values. Thus, adoption of high acid autoclave leaching, could dissolve uranium quite selectively from the liandratite phase.

### Conclusions

Leaching studies on different ores, having chemically refractory uranium minerals (betafite, liandratite) and on an ore where the uranium phases are in very-fine to ultra-fine dissemination in the host matrix, have indicated the scope of recovering uranium very efficiently, by using autoclave reactor. The investigations provide positive signals for exploration and exploitation even “difficult to process” uranium ores of India. This is a welcome technological advance, for augmenting the uranium resources, in order to meet the fuel demands of our ambitious nuclear power programme.

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### References