Pore Diffusion Controlled Leaching Model Incorporating Particle Size Distribution: A Case Study

K. Anand Rao and T. Sreenivas
Mineral Processing Division, BARC Hyderabad

and

A.K. Suri
Bhabha Atomic Research Centre

Abstract

High rock permeability and liberation of uranium minerals in coarser sizes render leaching kinetics of medium to high grade (>0.2% \(\text{U}_3\text{O}_8\)) uranium ores to be best described either by homogeneous or topochemical reaction models. But in case of low-grade uranium ores with very fine dissemination of uranium minerals, the rate controlling step is observed to be the process of diffusion of dissolved ions in liquid within pores of rock particles. In the present study, the experimental leaching data generated on a low grade uranium ore from Tummalapalle in Andhra Pradesh, India is described by a pore diffusion model integrating particle size distribution.

The Tummalapalle ore contains 0.01% pitchblende as uranium mineral in intimate association with pyrite. The gangue minerals are 83% carbonates, 11.3% quartz, 0.47% pyrite. The diffusion of leachant phases like \(\text{CO}_3^{2-}\) and \(\text{O}^-\) inside the ore particles and the counter current diffusion of the reaction product uranyl carbonate anions is assumed to be the rate controlling step. The Effective diffusivity (\(D_{\text{eff}}\)) in turn is a function of porosity and tortuosity of the ground ore particles. Experiments included variation of partial pressure of oxygen from 4.5 kg/cm\(^2\) to 6.5 kg/cm\(^2\), stirring speed between 573 rpm to 900 rpm, reaction temperature in the range 125\(^\circ\)C to 165\(^\circ\)C and average particle size from 25.8 \(\mu\) to 34.76 \(\mu\). Gates-Gaudin-Schumann size distribution was incorporated into the kinetic model developed and the effective diffusivity was computed for different combinations of experimental conditions. The effective diffusivity was found to be in the range 0.61 cm\(^2\)/s to 5.67 cm\(^2\)/s. It is observed to be increasing with increase in partial pressure of oxygen, increase in stirring speed, increase in temperature and decrease in average particle size. Arrhenius plot of \(\log(D_{\text{eff}})\) Vs \(1/T\) yielded activation energy of 3.27 kcal/mole, which qualifies the assumption of diffusion controlled mechanism. The calculated and experimental conversions of uranium with time were found to be in good agreement.

Keywords: Pore diffusion model; Particle size distribution; Tummalapalle uranium ore; Alkaline leaching; Diffusivity
Introduction

The demand for uranium is on steady increase in India in recent past due to setting-up of new nuclear power plants in various parts of the country. These requirements are planned to be met with a mix of indigenous resources and imports (Anon 2012). An outcome of this scenario is the expansion programmes of the existing mills at Jaduguda and Turamdih in Singhbhum and setting-up of the third uranium mill at Tummalapalle in Andhra Pradesh based on alkaline leaching technology. A kinetic model is developed to describe the leaching behaviour of uranium from the Tummalapalle ore. Results of this study are presented in the paper.

Alkaline leaching of uranium ores involve oxidation of uranium present in uraninite / pitchblende followed by its dissolution in carbonate solution. The macroscopic chemical reaction, combining both the above steps, is given by Eq.(1) (Merrit, 1970).

\[
\text{UO}_2 + \frac{1}{2} \text{O}_2 + 3 \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Na}_4\text{UO}_2(\text{CO}_3)_3 + 2\text{NaOH} \quad [1]
\]

The hydroxyl ion precipitates uranium back as Na2U2O7 according to Eq.(2), if not neutralized by sodium bicarbonate. The neutralization reaction is

\[
2\text{Na}_4\text{UO}_2(\text{CO}_3)_3 + 6\text{NaOH} \\
\rightarrow \text{Na}_2\text{U}_2\text{O}_7 + 6\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} \quad [2]
\]

\[
\text{NaOH} + \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \quad [3]
\]

The above chemical reactions during extraction of uranium into fluid phase from ground ore particles are controlled by various factors (1) degree of liberation of uranium in the ore, grain size of uranium, porosity of gangue as well as uranium minerals (2) type of leachant (3) type of oxidant and (4) system properties like temperature, pressure, stirring speed and type of stirrer, leachant vessel. If uranium minerals are fully liberated, the popular shrinking core model mechanisms (1) mass transport through the boundary layer fluid film surrounding each particle or (2) internal surface chemical reaction are applicable. If the product layer is porous, (3) core-shell (topochemical reaction model) diffusion, is applicable. Usually, the uranium minerals in the ground ore are fully / partially liberated by grinding. In high grade ores, even if uranium is partially liberated, the above mechanisms of shrinking core model generally fit the kinetic data. This is due to high rock permeability to the leachants (Barlett, 1971; Du Preez et al, 1981). But for low grade and finely disseminated uranium ores like Tummalapalle ore in Andhra Pradesh, no single mechanism of shrinking core model was found to be applicable. Earlier attempts to fit a shrinking core kinetic model to the leaching data obtained on this ore resulted in a mixed controlled model, initially chemical reaction and later shell diffusion controlled (Anand Rao, 2010). This could be due to low rock permeability of the rock. Low permeability is evident from the low average specific surface area (0.42 m²/g given in Table 1) and low pore volume (0.002 cm³/g given in Table 1). Transport of dissolved metal in liquid within pores of rock particles is likely to be rate controlling step in overall extraction process, especially for low grade ores (Roach et al, 1978). Counter current diffusion of uranyl anion out of the particle with CO3-2 and O-2 ions of the fluid phase diffusing into the particle is involved. The diffusivity in turn is a function of porosity and tortuosity of the ground ore particles. Hence, a pore diffusion rate controlling extraction kinetic model is presented herein for the case of low grade uranium ore from Tummalapalle, Andhra Pradesh, India.

Experimental

Materials

The low grade uranium ore from Tummalapalle, India is phosphatic silicious dolomitic limestone containing about 80% carbonates, 12% quartz, 1.2% pyrite as the main gangue minerals and 0.01% pitchblende in intimate association with pyrite. Due to high acid consuming gangue, the alkaline reagent, mixture of Na2CO3 and NaHCO3 dissolved in water, was used as leachant. Oxygen gas under pressure was used as oxidant.
A five litre capacity cylindrical shape autoclave made of stainless steel is used for carrying out kinetic tests of leaching. It is equipped with gas induction type hallow shaft fitted with 50 mm diameter single stage turbine type impeller, oxygen inlet pipe one end connected to oxygen cylinder through pressure reducing valve, cooling water coil, pressure sensor, rupture disk and a solenoid valve which releases pressure whenever exceeds the set point. Top lid of the vessel is coupled to motor drive with a magnetic seal and provided with a thermo well for thermocouple. Electrical heater along with insulation is wrapped outside the cylindrical vessel. Heater is connected to temperature indicator and controller to maintain constant temperature. Cooling water tank with pump is provided with auto mechanism of starting the pump whenever there is a rise in temperature due to exothermicity of the reactions inside the vessel.

**Method**

The Tummalapalle uranium ore was crushed to -1/4” size in a laboratory jaw crusher and then ground using ball mill for three different time periods to prepare different sized feed samples. The specific surface area determined by BET method using CO2 adsorption and the porosity determined by Mercury Porosimeter of the ore sample (-1/4”) are given in Table 1.

<table>
<thead>
<tr>
<th>Surface area (m²/g)</th>
<th>0.42</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.002</td>
</tr>
<tr>
<td>Pore dia.(μ) = 6 Pore Volume(c.c. / g) / Surface area(m² / g)</td>
<td>0.03</td>
</tr>
</tbody>
</table>

In each leaching experiment, dry ground ore (1 kg) and predetermined amount of tap water were placed in the autoclave. Autoclave lid was then closed; agitator started at low speed and heated up to 80° C, at which instance the reactor was pressurized to arbitrarily chosen pressure of about 3 kg/cm² using oxygen. The contents were then continued to be heated using electrical heater, which was set to the desired temperature (>1000°C). Incidental increase in pressure of the reactor was observed, while heating so. Required amounts of alkali reagents dissolved in small amount of water were loaded into the autoclave using positive displacement pump. The pressure of the reactor was increased to the desired total pressure using oxygen, the agitator motor was set to the desired stirring speed and the clock time noted as starting time of leaching experiment. Leaching continued for 6 hr. Slurry samples at time intervals of 1 hr, 2 hr, 4 hr and 6 hr were drawn, solids filtered out and the leach liquors were analysed for their $U_3O_8$ content by spectrophotometry. Solid samples at the end of 6 hr were also analysed for their $U_3O_8$ content. The average of back calculated feed values of $U_3O_8$ computed in all the experiments was used in calculating experimental conversion ($\alpha_{exp}$) with time in each leaching test.

The constant parameters and levels of the variable parameters of present study, given in Table 2, were fixed around the optimum values observed in previous studies (Suri et al, 2010) on Tummalapalle ore.

<table>
<thead>
<tr>
<th>Table 2 Constant and variable parameters of Tummalapalle ore leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constant Parameter</strong></td>
</tr>
<tr>
<td>Pulp density</td>
</tr>
<tr>
<td>$Na_2CO_3$</td>
</tr>
<tr>
<td>$NaHCO_3$</td>
</tr>
<tr>
<td><strong>Variable Parameter</strong></td>
</tr>
<tr>
<td>Partial pressure of oxygen, $P_0_2$ in kg/cm² (absolute)</td>
</tr>
<tr>
<td>Stirring speed, s in rpm</td>
</tr>
<tr>
<td>Particle Size, d in μ</td>
</tr>
<tr>
<td>Temperature, T in K</td>
</tr>
</tbody>
</table>

* The constant values used when the effect of other parameters was investigated

**Pore diffusion rate controlled extraction model**

The fraction of uranium extracted, $\alpha$, from a single spherical particle of radius $R_i$ in time $t$, is given by following Eq.(4) according to pore diffusion model (Jost, 1960; Perry, 1950).
\[
\alpha(t, R_i) = 1 - \frac{6}{\pi^2} \sum_{k=1}^{\infty} \left( \frac{1}{k^2} \pi^2 D_{\text{eff}} t / R_i^2 \right) \tag{4}
\]

where \( K = 1, 2, \ldots \) and \( D_{\text{eff}} = \text{Effective diffusivity which can be described by Eq.(5)}. \)

\[
D_{\text{eff}} = \frac{D_{AB} \varepsilon}{\tau_D} \tag{5}
\]

where, \( \varepsilon = \text{porosity and the } \tau_D = \text{tortuosity factor of the ground ore particle and } D_{AB} = \text{Diffusivity of solute A in solvent B}. \)

**Incorporating particle size distribution into the pore diffusion model**

Murhammer et al (1986) showed that the error obtained by assuming uniform particle size distribution (= average of minimum and maximum size) was less than 5%, only if the ratio of maximum to minimum particle size is less than 5 (Murhammer et al, 1986). Gbor et al (2004) showed that if coefficient of variation of particle size distribution following gamma function is more than 0.3, shrinking core model without considering particle size distribution would lead to substantial errors. Hence, the size distribution of ground ore particles is considered. Gates-Gaudin-Schumann (GGS) relation, the most common representation of particle size distribution, is given by Eqs.(6) and (7) (Kelly and Spottiswood, 1982).

\[
y(R_i) = \left( \frac{R_i}{R_{\text{max}}} \right)^m \tag{6}
\]

where \( y(R_i) \) is cumulative weight fraction finer than size \( R_i \) and \( R_{\text{max}} \) is size of largest particle. The fraction of material, \( \Delta y(R_i) \), in size range between \( R_i \) and \( R_i - \Delta R_i \) is obtained by differentiation of the above equation

\[
\Delta y(R_i) = \frac{m R_i^{m-1}}{R_{\text{max}}} \Delta R_i \tag{7}
\]

Sum of weight fractions of discrete size intervals between the smallest and largest size should be constrained to 1.

\[
\sum_{R_i=R_{\text{min}}}^{R_i=R_{\text{max}}} \Delta y(R_i) = 1 \tag{8}
\]

The cumulative fraction extracted after an extraction time period \( t \) is obtained by summation of products of fraction extracted in each size \( R_i \) according to Eq.(4) and the fraction of material in small interval size \( R_i \) and \( R_i - \Delta R_i \) according to Eq.(7),

\[
\alpha(t) = \sum_{R_i=R_{\text{min}}}^{R_i=R_{\text{max}}} \left( 1 - \frac{6}{\pi^2} \sum_{k=1}^{\infty} \left( \frac{1}{k^2} \pi^2 D_{\text{eff}} t / R_i^2 \right) \right) \Delta y(R_i) \tag{9}
\]

**Fitting experimental data**

The fractional conversion (\( \alpha_{\text{exp}} \)) was calculated using the average back calculated feed assay, 737 ppm U3O8, obtained from residue assay and leach liquor assay in each experiment and the leach liquor concentration measured at different time intervals in all the experiments.

\[
\alpha_{\text{exp}} = \frac{C V}{W f}
\]

where, \( C = \text{Concentration of U}_3\text{O}_8 \text{ in the leach liquor at time } t, \text{g/L} \)

\( V = \text{Volume of leach liquor} = 0.9 \text{ L} \)

\( W = \text{weight of feed} = 1000 \text{ g} \)

\( f = \text{average %}U_3\text{O}_8 \text{ in the feed} = 0.0737 \)

Sieve analysis data of three feed samples are fitted by GGS distribution function according to Eq.(6) as shown in Fig.1. The plots of all the three products yielded a liner relation with high degree of correlation. From the slope and intercept values of straight lines obtained in Fig.1, the values of \( m \) and \( R_{\text{max}} \) corresponding to three different sized feed samples are tabulated in Table 3.
Eq.(9) can be solved for the only unknown $D_{\text{eff}}$ for each set of leaching conditions. In order to fit the experimental data to this model equation, a computer program is written to find the effective diffusion coefficient, $D_{\text{eff}}$, in each experiment. Using $m$ and $R_{\text{max}}$ values of the feed sample used in each experiment, the value of $\Delta y(R_i)$ is computed according to Eq.(7) for each $R_i$, using 600 values of $R_i = R_{\text{max}}/600$ to $R_{\text{max}}$ with step size of $R_{\text{max}}/600$, and stored. The step size used was found to be lower enough to meet the constraint stated as Eq.(8). For a value of $t$, for which $\alpha_{\text{exp}}$ is available, sum of the terms of infinite series in Eq.(9) is approximated to a finite series sum such that values of $K$ ranged from 1 to $k$ where $k$ is the least value of $K$ whose term in the sum is less than 0.0005 of the cumulative sum of all previous terms. The omitted terms in the finite series make a negligible contribution to the sum. For each value of $t$, the cumulative conversion, $\alpha(t)$ was computed by summing the product of $\alpha(t,R_i)$ and $\Delta y(R_i)$ over all the values of $R_i$ (no. of $R_i$ values being 600 as indicated above). Value of $D_{\text{eff}}$ is calculated to minimize the error given by

$$\text{Error} = \sum_{1}^{N_{\text{m}}} (\alpha_{\text{exp}} - \alpha_{\text{cal}})^2$$

where $\alpha_{\text{exp}}$ is the experimental value of fractional conversion, $\alpha_{\text{cal}}$ is the calculated value of fraction reacted using Eq.(9), and $N_{\text{m}}$ is the total number of data, which is 4 in the present case, as $\alpha_{\text{exp}}$ in each kinetic experiment is available for four time periods of leaching.

---

**Table 3: Particle size distribution parameters of Tummalapalle ore samples used in leaching experiments**

<table>
<thead>
<tr>
<th>$R_{\text{av}}$ ($\mu$)</th>
<th>Gates Gaudin Schumann distribution parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.4</td>
<td>$m = 0.46$, $R_{\text{max}} = 54$</td>
</tr>
<tr>
<td>16.2</td>
<td>$m = 0.56$, $R_{\text{max}} = 79$</td>
</tr>
<tr>
<td>17.4</td>
<td>$m = 0.62$, $R_{\text{max}} = 83$</td>
</tr>
</tbody>
</table>

---

**Fig. 1:** Gates Gaudin Schuhmann plots of three feeds of Tummalapalle ore generated with different time periods of grinding.
Table 4: Results of kinetic leaching experiments on Tummalapalle ore along with calculated Diffusivity ($D_{eff}$ cm/min) and conversion of $U_3O_8$

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Partial Pressure of $O_2$</th>
<th>$P_{O_2}$ at temp. $T$</th>
<th>Total pressure, $P_{total}$</th>
<th>Stirring speed, $s$</th>
<th>Average particle radius, $R_{av}$</th>
<th>Temp., $T$</th>
<th>$D_{eff} \times 10^{11}$ (calculated)</th>
<th>Time, $t$</th>
<th>Conversion of $U_3O_8$, $\alpha_{exp}$</th>
<th>Conversion of $U_3O_8$, $\alpha_{cal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.5</td>
<td>2.3</td>
<td>5.8</td>
<td>764</td>
<td>12.4</td>
<td>398</td>
<td>0.607</td>
<td>1</td>
<td>0.5</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.59</td>
<td>0.61</td>
</tr>
<tr>
<td>2*</td>
<td>5.5</td>
<td>2.3</td>
<td>6.8</td>
<td>764</td>
<td>12.4</td>
<td>398</td>
<td>2.43</td>
<td>1</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.71</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.74</td>
<td>0.76</td>
</tr>
<tr>
<td>3</td>
<td>6.5</td>
<td>2.3</td>
<td>7.8</td>
<td>764</td>
<td>12.4</td>
<td>398</td>
<td>2.43</td>
<td>1</td>
<td>0.65</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.67</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.75</td>
<td>0.76</td>
</tr>
<tr>
<td>4</td>
<td>5.5</td>
<td>2.3</td>
<td>6.8</td>
<td>573</td>
<td>12.4</td>
<td>398</td>
<td>2.025</td>
<td>1</td>
<td>0.61</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.69</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.71</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>0.73</td>
<td>0.78</td>
</tr>
<tr>
<td>5</td>
<td>5.5</td>
<td>2.3</td>
<td>6.8</td>
<td>900</td>
<td>12.4</td>
<td>398</td>
<td>2.835</td>
<td>1</td>
<td>0.67</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.73</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.74</td>
<td>0.77</td>
</tr>
<tr>
<td>6</td>
<td>5.5</td>
<td>3.6</td>
<td>8.1</td>
<td>764</td>
<td>12.4</td>
<td>413</td>
<td>2.835</td>
<td>1</td>
<td>0.69</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.74</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.73</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>0.75</td>
<td>0.81</td>
</tr>
<tr>
<td>7</td>
<td>5.5</td>
<td>7.0</td>
<td>11.5</td>
<td>764</td>
<td>12.4</td>
<td>438</td>
<td>5.67</td>
<td>1</td>
<td>0.78</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.76</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.81</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>0.82</td>
<td>0.88</td>
</tr>
<tr>
<td>8</td>
<td>5.5</td>
<td>2.3</td>
<td>6.8</td>
<td>764</td>
<td>17.4</td>
<td>398</td>
<td>0.957</td>
<td>1</td>
<td>0.43</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.47</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.48</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>0.54</td>
<td>0.56</td>
</tr>
<tr>
<td>9</td>
<td>5.5</td>
<td>2.3</td>
<td>6.8</td>
<td>764</td>
<td>16.2</td>
<td>398</td>
<td>1.435</td>
<td>1</td>
<td>0.47</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0.55</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>0.51</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>0.55</td>
<td>0.61</td>
</tr>
</tbody>
</table>

*Base experiment, conducted at the constant values of each variable, when other parameters are changed
Results and Discussion

The values of $D_{\text{eff}}$ computed using Eq.(11) and corresponding values of $\alpha_{\text{cal}}$ along with the set of experimental conditions of each experiment are given in Table 4. The predicted and experimental conversion values of U3O8 given in Table 4 are plotted as a parity plot in Fig.2.

**Effect of temperature**

Effective diffusivity is found to be increasing with increase in temperature. Arrhenius plot of $\log(D_{\text{eff}})$ Vs $1/T$, given in Fig.3, has yielded activation energy($E_a$) of 3.27 kcal/mole. Less than 5 kcal/mole of Arrhenius activation energy cross validates the assumption of diffusion controlled mechanism (Laidler, 1965).

![Fig.3: Arrhenius plot of Diffusivity for leaching of Tummalapalle uranium ore](image)

**Effect of partial pressure of oxygen**

The effective diffusivity is found to be increasing from $0.61 \times 10^{-11}$ cm$^2$/s to $2.43 \times 10^{-11}$ cm$^2$/s when partial pressure of oxygen increased from 4.5 kg/cm$^2$ to 6.5 kg/cm$^2$. This could be due to increase in solubility of oxygen with the increase in partial pressure of oxygen leading to increased concentration gradient between the bulk of the solution and the mineral surface.

**Effect of stirring speed**

Effective diffusivity is found to be increasing from $2.03 \times 10^{-11}$ to $2.84 \times 10^{-11}$ cm$^2$/s with increase in stirring speed from 573 to 900 rpm which could be due to increased rate of diffusion at higher agitation speeds.

**Effect of particle size**

The effective diffusivity is found to be decreasing with increase in particle size. The algebraic function is however incorporated in the leaching model given in Eq.(9).

**Conclusion**

Pore diffusion model coupling particle size distribution has been applied to the data generated on carbonate leaching of Tummalapalle uranium ore. The effective diffusivities of the solutes during leaching under different process conditions of leaching were estimated. The variables studied included partial pressure of oxygen (4.5 to 6.5 kg/cm$^2$), stirring speed (573 to 900 rpm), different particle size distributions with maximum particle radius from 54 to 83µ and
temperature 398 to 438 K. The effective diffusion coefficient in leaching of Tummalapalle uranium ore was found to be in the range 0.6x10^{-11} \text{ cm}^2/\text{s} to 5.67x10^{-11} \text{ cm}^2/\text{s}.

**Acknowledgements**

The authors thank the staff of Mineralogy Petrology group of Atomic Minerals Directorate for Exploration and Research, Hyderabad for ore microscopy studies. They also acknowledge services of Chemical Lab, Mineral Processing Division, Bhabha Atomic Research for timely chemical analyses. Authors wish to thank Dr. J.K. Chakravartty, Director, Materials Group, Bhabha Atomic Research Centre for his encouragement during the investigations.

**Nomenclature**

- \( C \): concentration of uranium in leach liquor at time \( t \), g/L
- \( D_{\text{eff}} \): effective diffusion coefficient for diffusion in a porous solid, cm²/s
- \( D_{\text{AB}} \): ordinary diffusion coefficient for molecular diffusion in a fluid phase, cm²/s
- \( E_a \): Arrhenius activation energy, kcal/mole
- \( \varepsilon \): porosity of the particle - volume fraction of pore space
- \( f \): feed assay \( \text{U}_3\text{O}_8 \), percent
- \( K \): integer index, integer
- \( m \): particle size parameter of the Gates Gaudin Schuhmann function
- \( R_i \): radius of ith uranium ore particle, µ
- \( R_{\text{min}} \): radius of smallest uranium ore particle, µ
- \( R_{\text{max}} \): radius of largest uranium ore particle, µ
- \( T \): reaction temperature, °K
- \( t \): reaction time, h
- \( s \): stirring speed, rpm
- \( \tau_D \): tortousity factor for diffusion in pores (usually \( = 2 \))
- \( y(R) \): cumulative weight fraction of ore particles finer than radius \( R \), fraction
- \( \Delta y(R_i) \): fraction of particles in size range between \( R_i \) and \( R_i + \Delta R_i \), fraction
- \( V \): volume of leach liquor, L
- \( W \): weight of feed, g

**Greek Letters**

- \( \alpha(t, R) \): fractional conversion of uranium ore particle of radius \( R \) at time \( t \), fraction
- \( \alpha_{\text{cal}} \): calculated value of fraction of uranium reacted, fraction
- \( \alpha_{\text{exp}} \): experimental value of fraction of uranium reacted, fraction

**References**


5. Gbor, P.K., Jia, C.Q., 2004. Critical evaluation of coupling particle size distribution with the
shrinkin...g core model, Chemical Engineering Science 59, 1979-1987.