CHAPTER 7. Dissolution kinetics of UO$_2$-PuO$_2$ MOX pellets in nitric acid medium

7.1 Introduction
The primary aim of this research work, as mentioned in section 1.10, is to determine the intrinsic dissolution kinetics of typical FBR driver fuel (plutonium rich urania plutonia MOX fuel) under PUREX process conditions. The dissolution kinetics of UO$_2$ and simulated urania ceria MOX pellets have already been explained in detail in Chapters five and six. Their kinetic parameters have been evaluated under typical PUREX process conditions which were used as the basis for studying the kinetics of FBR plutonium rich MOX fuel. As explained already in section 6.1, we could not afford to carry out many experiments with plutonium fuel system. Hence based on the results of the experiments on UO$_2$ and urania ceria MOX pellet dissolution in nitric acid and with minimum number of experiments on urania plutonia MOX fuel pellets, the kinetics of dissolution of urania plutonia MOX fuel in nitric acid was studied and modeled. This chapter presents the MOX dissolution studies in detail.

7.2 Nature of fuel pellets
The MOX pellets required for the study were brought from BARC, Mumbai. These represent typical inner core PFBR MOX fuel pellets, whose composition is 21.78 mass percent of PuO$_2$ and the rest is UO$_2$ ((U$_{0.782}$Pu$_{0.218}$)O$_2$). All the pellets had an annular hole at the centre to decrease the difference between the centre line and surface temperature within each pellet during its irradiation in PFBR (refer Fig. 4.3). All these pellets were dimensionally rejected due to some minor crack/chipping along its surface. The physical features of the pellet used in the experiments are given in Table 7.1.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameter</th>
<th>Approximate Details</th>
</tr>
</thead>
<tbody>
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<td>Weight (g)</td>
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</tr>
<tr>
<td>2</td>
<td>Diameter (mm)</td>
<td>5-6</td>
</tr>
<tr>
<td>3</td>
<td>Length (mm)</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Annular hole diameter (mm)</td>
<td>1-2</td>
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</table>
7.3 Erection of the experimental set-up

A glass dissolver similar to that used for UO₂ and simulated urania ceria MOX pellets was used for studying the dissolution behaviour of MOX pellets in nitric acid. The design and construction of the dissolution vessel is already explained in section 5.1. The entire dissolution reactor along with the glass impeller for stirring, off-gas condenser, off-gas scrubber, heating mantle with temperature controller etc were installed inside an airtight glove box. The services required for the experimental studies like air-ejector for sucking the off-gas etc. were erected inside a fume hood adjacent to the glove box. Permanent SS lines were laid between the fume hood and glove box for connecting the required services to the experimental set-up. Prior to the experiments, the erected experimental setup was inspected and cleared by the competent safety authority of IGCAR. The schematic sketch of the experimental set-up is shown in Fig. 7.1.

Fig. 7.1. Schematic sketch of the dissolution set-up for dissolving MOX pellets

7.4 Effect of initial concentration of nitric acid on the dissolution kinetics

Similar to the experimental studies on the dissolution behaviour of UO₂ and simulated MOX pellets in nitric acid, initial set of experiments were carried out to study the effect of initial concentration of nitric acid on the dissolution kinetics of MOX pellets at 353 K. Experiments were conducted at initial concentrations of nitric acid of 8, 10, 11.5 and 16 M. The agitation rate and temperature were maintained constantly at 600 RPM and 353 K.
as justified in sections 5.2 and 5.5.3 respectively. The graphical representation of the effect of initial concentration of nitric acid on the dissolution of MOX pellets is shown in Fig. 7.2.

**Fig. 7.2. Effect of initial acidity on the dissolution kinetics of (U\textsubscript{0.782}Pu\textsubscript{0.218})O\textsubscript{2} MOX pellet at 353 K and 600 RPM**

![Graph showing dissolution kinetics](image)

Fig. 7.2 clearly shows that the increase in the initial concentration of nitric acid leads to an increase in the rate of dissolution. Similar to UO\textsubscript{2} and simulated MOX pellets, all these dissolution curves exhibit the sigmoidal shape indicating the presence of an autocatalytic effect. This is due to the autocatalytic dissolution of UO\textsubscript{2}, the major component of the MOX pellets (78.28 wt %). A more interesting and unique behaviour among the fuels used for the present investigations was observed for the urania plutonia MOX pellets. In all the above experiments it was found that uranium always got leached out of the pellet faster than plutonium. This was unlike the case of simulated MOX pellets wherein the uranium and cerium composition in the liquid was always the same and equal to that of the initial pellet. This behaviour of MOX pellet is indicated in Fig. 7.3 which typically shows the percentage dissolution of uranium and plutonium separately and together during the dissolution of urania plutonia MOX pellets in 8 M nitric acid at 353 K.
Fig. 7.3 clearly brings out the relative difference in the rate of dissolution of uranium and plutonium from the MOX pellet. Though plutonia dissolves sluggishly when compared to urania as shown here, the very fact that the pellet ultimately dissolves completely re-emphasizes that MOX pellets with plutonium below 35 wt % dissolves completely just by heating in pure nitric acid without the requirement of any other strong oxidizing or reducing agents as mentioned in the literature. This behaviour was seen during all the dissolution experiments of urania plutonia MOX pellets in nitric acid carried out as a part of this research work.

The consolidated results of the effect of initial concentration of the acid on the dissolver solution composition are shown in Fig. 7.4. It could be clearly understood from Fig.7.4 that as the concentration of acid increases, the rate of plutonium oxide dissolution increases more than that of uranium oxide. Hence the gap between the percentage uranium and percentage plutonium curve under the given condition narrows gradually with the increase in the initial concentration of nitric acid. All of these data were used for the evaluation of the kinetic parameters of the dissolution of MOX pellets in nitric acid during the modeling of the reaction kinetics.
Fig. 7.4. Effect of acidity on the composition of the dissolver solution during the dissolution of (U$_{0.782}$Pu$_{0.218}$)O$_2$ MOX pellet at 353 K and 600 RPM

![Graph showing the effect of acidity on the composition of the dissolver solution during the dissolution of (U$_{0.782}$Pu$_{0.218}$)O$_2$ MOX pellet at 353 K and 600 RPM.]

Fig. 7.5. Effect of acidity on the relative dissolution of uranium and plutonium from (U$_{0.782}$Pu$_{0.218}$)O$_2$ MOX pellet at 353 K and 600 RPM

![Graph showing the effect of acidity on the relative dissolution of uranium and plutonium from (U$_{0.782}$Pu$_{0.218}$)O$_2$ MOX pellet at 353 K and 600 RPM.]

As described already, the composition of the urania plutonia MOX pellets used in the
dissolution studies is 78.22% uranium and 21.78% Pu. Hence the ratio of weight percent of uranium to plutonium in all the pellets is about 3.5872 (78.2/21.8). Therefore for better understanding of the differential dissolution rate of urania and plutonia from the same MOX pellet, the mole ratio of U to Pu in solution was plotted against time for each of the above experiment and is shown in Fig. 7.5. The lowest value of 3.6 on the y axis in Fig. 102 corresponds to the U/Pu mole ratio of the starting pellet. It could be seen that in all the cases, this value is reached only at the end of the dissolution. Prior to that, this value starts from a much higher number before gradually reaching 3.6 at the end. This translates into the fact that the mole ratio of uranium to plutonium in the solution during the course of dissolution is always higher than that in the starting pellet. That is uranium dissolves more rapidly than plutonium at the start of the dissolution experiment and the rate of plutonium dissolution gradually picks up till their mole ratio reaches a value similar to that in the starting pellet. It should also be noted that this mole ratio at any given time during the course of dissolution is always inversely proportional to the initial concentration of nitric acid. These experimental data were later used in deriving the model equations for the dissolution of MOX pellets in nitric acid which was subsequently employed to determine the kinetic parameters using non-linear regression techniques.

The consolidated results of the effect of initial concentration of nitric acid on the dissolution of MOX pellets is given in Fig. 7.6 by making a parity plot of % uranium and % plutonium against the total % dissolution for each of the condition. The centre most dotted line in Fig. 7.6 corresponds to the composition of uranium and plutonium in the MOX pellet. It could be noted that the percentage uranium dissolution line under the given condition always lies above and the plutonium line always below the centre line. Thus the composition of uranium in the dissolved solution is always higher than that in the starting MOX pellet at any stage of the dissolution reaction. The more the gap between the % uranium and % plutonium line under the given condition, faster would be the dissolution of urania when compared to plutonia from the pellet. It could be clearly seen that this gap decreases gradually as the initial concentration of nitric acid is increased. This reconfirms two facts; from the same MOX pellet (i) the dissolution of urania is rapid when compared to plutonia and (ii) with increase in the initial concentration of nitric acid, the rate of dissolution of plutonia increases more when compared to urania. The relative rate of dissolution of the MOX pellets with respect to the concentration of nitric acid is clearly shown in the inset of Fig. 7.6.
Along the diagonal of the inset from bottom right to the top left, the top four lines are that of urania and the bottom four are that of plutonia. Among the four urania lines, the order of initial concentration of nitric acid increases from top to bottom, whereas in the case of plutonia, the order is reversed. Hence in general, as the initial concentration of nitric acid increases the corresponding lines of % uranium dissolution and % plutonium dissolution comes closer. This indicates that with increase in acidity, the difference in the rates of UO$_2$ and PuO$_2$ from the MOX pellet decreases.

7.5 Effect of temperature on the dissolution kinetics of MOX

The next parameter which was chosen to study its effect on the MOX pellet dissolution kinetics was temperature. For this purpose, the acidity and the mixing rate was fixed at 8 M and 600 RPM as described in Chapter 5. The temperature was changed from 348 K to 368 K in steps of 5 K. Thus five different temperatures were chosen. The experiments were carried out in the same set-up as explained in the previous section. The results are presented graphically in Fig. 7.7. The following are some of the salient features of the results presented in Fig. 7.7.
a. Like all other previous experiments, these dissolution experiments also exhibit the sigmoidal shape for the conversion curve indicating the presence of autocatalytic effect of nitrous acid on UO$_2$ dissolution.

b. As the temperature is increased, the S shape of the curve gradually reduces. This is due to the increased instability of nitrous acid at higher temperature leading to the gradual decrease in its autocatalytic effect.

**Fig. 7.7. Effect of temperature on the dissolution kinetics of (U$_{0.78}$Pu$_{0.21}$)O$_2$ MOX pellet in 8 M HNO$_3$ and 600 RPM**

Similar to the results of the experiments to study the effect of initial concentration of nitric acid, in these experiments also it was found that UO$_2$ preferentially got leached faster than PuO$_2$. The difference between the rate of dissolution of UO$_2$ and PuO$_2$ was found to reduce as the temperature was increased which is shown in Fig. 7.8.

Though the experiments were carried out at five different temperature, Fig. 7.8 shows the percentage dissolution of urania, plutonia and the total pellet at only three different temperatures as the lines would overlap and make the graph complicated if all were included. The most striking feature of Fig. 7.8 was the reduction in the gap between the % uranium and % plutonium lines as the temperature was increased. The relative dissolution of uranium and plutonium from the MOX pellets as a function of temperature is shown more clearly in Fig. 7.9.
Fig. 7.8. Effect of temperature on the composition of the dissolved solution during the dissolution of \((U_{0.782}Pu_{0.218})O_2\) MOX pellet in 8 M HNO₃ at 600 RPM

![Graph showing the effect of temperature on the dissolution of MOX pellet.]

Fig. 7.9. Effect of temperature on the relative dissolution of uranium and plutonium from \((U_{0.782}Pu_{0.218})O_2\) MOX pellet at 8 M nitric acid and 600 RPM

![Graph showing the ratio of U to Pu dissolution over time at different temperatures.]

It could be noted from Fig. 7.9 that as the temperature is increased, the difference in the relative dissolution of urania and plutonia in the MOX pellet decreases. This is indicated by the decrease in the ratio of % U dissolved to % Pu dissolved at any given time as a
function of increasing temperature.

The same information is given in Fig. 7.10 as well, wherein the percentage uranium and plutonium dissolved were plotted against the total percentage dissolved for all the temperatures. As the temperature is increased, the gap between the percentage uranium line and the percentage plutonium line decreases. This is a fair indication that the increase in the rate of plutonia dissolution is higher when compared to urania as the temperature is increased.

Fig. 7.10. Consolidated effect of temperature on the dissolution of \((U_{0.782}Pu_{0.218})O_2\) MOX pellet at 8 M nitric acid and 600 RPM with expanded view in the inset

7.6 Effect of mixing on the dissolution kinetics of MOX pellets in nitric acid

Experiments were conducted in a similar fashion to study the effect of mixing intensity on the dissolution kinetics of MOX pellets in nitric acid after understanding the effect of initial acid concentration and temperature. Four different mixing rates were employed for this purpose, namely, 0, 100, 600 and 1500 RPM. The results of the experiments are shown graphically in Fig. 7.11. It could be seen from the Fig. that, as the mixing rate is increased, the rate of dissolution decreases which is similar to the case of UO\(_2\) and simulated urania ceria MOX pellets under the same conditions. It could also be noted that
the difference in the dissolution rate while increasing the mixing rate from 600 and 1500 RPM is negligible. Hence, similar to the case of UO$_2$ and simulated urania ceria MOX pellets the effect of diffusion from 600 RPM and at further higher mixing rate is at its barest minimum. Therefore the kinetic parameters to be evaluated under these conditions would be intrinsic in nature.

**Fig. 7.11. Effect of mixing on the dissolution kinetics of (U$_{0.782}$Pu$_{0.218}$)O$_2$ MOX pellet in 8 M nitric acid at 80°C**

![Graph showing the effect of mixing on dissolution kinetics](image)

The effect of mixing intensity on the rate of dissolution of urania and plutonia in the MOX pellet is shown in Fig. 7.12. Though four different mixing rates were employed, only two were shown in this Fig. for the sake of simplicity. Otherwise the figure would become more complicated due to overlapping of curves of one mixing rate with the other when the results of all the four mixing rates were included in the same figure. It could be understood from Fig. 108 that, similar to urania, the rate of dissolution of plutonia was also found to be inversely proportional to the rate of mixing. The presence of nitrous acid is not expected to make any difference to the rate of dissolution of plutonia in nitric acid as the oxidation state of plutonium remains the same in both the solid and liquid phases during the dissolution. Hence the mixing intensity is expected to be directly proportional to the rate of dissolution of plutonia similar to any solid dissolving in a liquid medium. This contradicting observation could be explained based on the behaviour of urania. As
explained in Chapter 5, the rate of dissolution of urania is inversely proportional to the rate of mixing due to the catalytic effect of nitrous acid which is present more at the vicinity of the pellet surface at lower mixing rate. Urania being the major component of the MOX pellet, its faster dissolution rate at lower mixing rate renders the pellet more porous. This increases the effective surface area of the pellet leading to better contact between the pellet and acid resulting in the increased rate of dissolution of plutonia. This could be inferred from Fig. 7.12 by the sudden increase in the slope of the plutonia dissolution line when sufficient urania has got dissolved as the mixing intensity is decreased.

**Fig. 7.12. Effect of mixing rate on the rate of dissolution of UO₂ and PuO₂ in**

\[(U_{0.782}\text{Pu}_{0.218})O_2\] MOX pellet in 8 M HNO₃ at 353 K

For better understanding, the effect of mixing on the relative dissolution of urania and plutonia from the same MOX pellet is given in Fig. 7.13 in terms of ratio of molar concentration of uranium to plutonium in the solution as a function of time for all the mixing rates employed. The lowest point in the y axis of Fig. 7.13 corresponds to 3.556 which is the molar ratio of uranium to plutonium in the starting MOX pellet. It could well be understood from the Fig. that at reduced mixing rate, urania dissolves relatively much faster that plutonia which is reflected by the high molar ratio of uranium to plutonium in the solution. As the mixing rate is increased, this value gradually approaches to that of the initial pellet at the end of dissolution. The curves at 600 and 1500 RPM are almost the
same indicating the negligible presence of diffusion control from 600 RPM and upwards.

**Fig. 7.13. Effect of mixing rate on the relative dissolution of uranium and plutonium from \((U_{0.782}Pu_{0.218})O_2\) MOX pellet in 8 M nitric acid at 353 K**

![Graph showing the effect of mixing rate on the dissolution of uranium and plutonium from an MOX pellet.](image)

**Fig. 7.14. Consolidated effect of mixing rate on the dissolution of \((U_{0.782}Pu_{0.218})O_2\) MOX pellet in 8 M nitric acid at 353 K**

![Graph showing the consolidated effect of mixing on the dissolution kinetics of urania plutonia MOX pellet.](image)

The consolidated effect of mixing on the dissolution kinetics of urania plutonia MOX pellet is given in Fig. 7.14. The construction of Fig. 7.14 is very similar to that of Figures 215.
7.6 and 7.10 except for the fact that the influencing parameter here is the mixing rate. All the above results of dissolution studies of \((U_{0.782}Pu_{0.218})O_2\) MOX pellet in nitric acid has brought out clearly the effect of various parameters on the reaction kinetics. All these experimental data were used for modeling the reaction kinetics. All these results makes an interesting case to study the effect of plutonium composition in the MOX pellet on its dissolution kinetics in nitric acid medium under various conditions. Similar studies on MOX pellets of other compositions would be performed, once they become available.

7.7 Evaluation of dissolution kinetics of \(UO_2-PuO_2\) fuel pellets

7.7.1 Introduction
The methodology adopted for modeling the dissolution of urania plutonia MOX pellets in nitric acid was similar to the methods which were already developed for understanding the dissolution behavior of simulated urania ceria MOX pellets in nitric acid presented in section 6.9 of this thesis.

7.7.2 Methodologies
The analytical methods employed for analyzing the dissolution behavior of urania ceria MOX pellets in nitric acid was employed for evaluating the kinetics of dissolution urania plutonia MOX pellets in nitric acid also.

7.7.2.1. Method 1 – Based on surface penetration of nitric acid into solid pellets
In this method, dissolution reaction is expressed by a two-step scheme as given below.\(^2\)

\[ W_{ue} \rightarrow W_e \rightarrow W_d \quad (7.1) \]

Where \(W_{ue}\) is the unexposed mass of fuel, \(W_e\) is the exposed mass and \(W_d\) the dissolved mass. The first process in the above equation is the penetration process. The rate of penetration process may be proportional to the concentration of nitric acid in the solution. The latter process in the above equation is considered as the chemical reaction. The reactions between \(UO_2\) and ions in the nitric acid solution under these experimental conditions were assumed as follows.\(^3, 4\)
The reactions between PuO$_2$ and ions in the nitric acid solution under these experimental conditions was assumed as

$$\text{PuO}_2 + 4\text{HNO}_3 \xrightarrow{k_{\text{Pu}}} \text{Pu(NO}_3\text{)}_4 + 2\text{H}_2\text{O}$$  \hspace{1cm} (7.5)

7.7.2.1.1. Case-I: Considering the effect of nitrous acid to be negligible

The dissolution experiments on urania plutonia MOX pellets in nitric acid was conducted at high stirring speed (600 rpm). Hence the concentration of HNO$_2$ at solid-liquid interface is very much less. So the dissolution of UO$_2$ due to nitrous acid could be neglected (equation 7.3 is not considered).

The rate equations obtained based on eqn(7.2), eqn(7.4) and eqn(7.5) are given by

$$\frac{dW_{\text{we}}}{dt} = -k_p[H\text{NO}_3]W_{\text{we}}$$  \hspace{1cm} (7.6)

$$\frac{dW_e}{dt} = k_p[H\text{NO}_3]W_{\text{we}} - \left( k_h[H\text{NO}_3]^2 + k_c[H\text{NO}_3]^2[U\text{O}_2^{2+}] + k_{e\text{c}}[H\text{NO}_3]^2 \right)W_e$$  \hspace{1cm} (7.7)

$$\frac{d[U\text{O}_2^{2+}]}{dt} = (MV)^{-1} \left( k_h[H\text{NO}_3]^2 + k_c[H\text{NO}_3]^2[U\text{O}_2^{2+}] \right)W_e$$  \hspace{1cm} (7.8)

$$\frac{d[\text{Pu}^{4+}]}{dt} = (MV)^{-1} \left( k_{\text{Pu}}[H\text{NO}_3]^2 \right)W_e$$  \hspace{1cm} (7.9)

$$\frac{d[H\text{NO}_3]}{dt} = -\left[ MV \right]^{-1} \left( 3k_h[H\text{NO}_3]^2 + 3k_c[H\text{NO}_3]^2[U\text{O}_2^{2+}] + 4k_{\text{Pu}}[H\text{NO}_3]^2 \right)W_e$$  \hspace{1cm} (7.10)

Where $k_p$ is the rate constant for the penetration process, $M$ is the molecular weight of mixed oxide and $V$ is the volume of the reacting solution.
The experimental data of concentrations of nitric acid, uranium and plutonium as a function of time were fitted into the above rate equations using a nonlinear regression technique to obtain rate constant that best correlates the experimental data. The best values were obtained by minimizing the following objective function

\[
f = \sum_{i=1}^{n} 20 \left( C_{Uexp} - C_{Ucalc} \right)^2 + \sum_{i=1}^{n} \left( C_{HNO_3exp} - C_{HNO_3calc} \right)^2 + \sum_{i=1}^{n} 20 \left( C_{Puexp} - C_{Pu calc} \right)^2 \quad (7.11)
\]

The rate constants \( k_p, k_h, k_c \) and \( k_{Pu} \) were calculated at different conditions of temperature and acidity. The values of rate constants and corresponding standard deviation are given in Table 7.2.

### Table 7.2. Rate constants for the dissolution of MOX fuel at different temperatures

<table>
<thead>
<tr>
<th>T(K)</th>
<th>348</th>
<th>353</th>
<th>358</th>
<th>368</th>
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<tr>
<td>( k_p ) ([L/mol]/min)</td>
<td>4.05E-04</td>
<td>4.97E-04</td>
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<tr>
<td>( k_h ) ([L/mol]^2/min)</td>
<td>3.17E-05</td>
<td>2.43E-05</td>
<td>1.81E-05</td>
<td>2.54E-05</td>
</tr>
<tr>
<td>( k_c ) ([L/mol]^3/min)</td>
<td>1.05E-04</td>
<td>2.54E-04</td>
<td>2.98E-04</td>
<td>3.83E-04</td>
</tr>
<tr>
<td>( k_{Pu} ) ([L/mol]^3/min)</td>
<td>1.06E-05</td>
<td>1.46E-05</td>
<td>1.42E-05</td>
<td>1.88E-05</td>
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<tr>
<td>sd(U)</td>
<td>0.0176</td>
<td>0.0083</td>
<td>0.0099</td>
<td>0.0109</td>
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<tr>
<td>sd(HNO_3)</td>
<td>0.0832</td>
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<td>0.0449</td>
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<tr>
<td>sd(Pu)</td>
<td>0.0085</td>
<td>0.0092</td>
<td>0.0094</td>
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### Table 7.3. Rate constants for the dissolution of MOX fuel at different acidity

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<th>[HNO_3] (M)</th>
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<tr>
<td>( k_p ) ([L/mol]/min)</td>
<td>5.30E-03</td>
<td>4.97E-04</td>
<td>4.11E-04</td>
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<td>( k_h ) ([L/mol]^2/min)</td>
<td>5.13E-06</td>
<td>2.43E-05</td>
<td>1.98E-05</td>
<td>1.48E-05</td>
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<tr>
<td>( k_c ) ([L/mol]^3/min)</td>
<td>3.57E-04</td>
<td>2.54E-04</td>
<td>2.53E-04</td>
<td>2.77E-04</td>
</tr>
<tr>
<td>( k_{Pu} ) ([L/mol]^3/min)</td>
<td>5.25E-06</td>
<td>1.46E-05</td>
<td>1.24E-05</td>
<td>1.21E-05</td>
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<tr>
<td>sd(U)</td>
<td>0.0108</td>
<td>0.0083</td>
<td>0.008</td>
<td>0.0105</td>
</tr>
<tr>
<td>sd(HNO_3)</td>
<td>0.0298</td>
<td>0.0359</td>
<td>0.0312</td>
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<tr>
<td>sd(Pu)</td>
<td>0.0063</td>
<td>0.0092</td>
<td>0.0068</td>
<td>0.0089</td>
</tr>
</tbody>
</table>

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The concentration profiles of uranium, nitric acid and cerium during the course of dissolution were determined using the model equations 7.6 to 7.10. The comparison between experimental and calculated values of [U(VI)], [HNO\textsubscript{3}] and [Pu] vs time at 348 K were shown as a semi log plot in the Figures 7.15 to 7.17. Similar plots were also generated for each of the conditions mentioned in the two tables given above.

**Fig. 7.15.** Modelled uranium concentration profile for the dissolution of 
(U\textsubscript{0.78}Pu\textsubscript{0.22})O\textsubscript{2} MOX pellet in 8 M HNO\textsubscript{3} at 348 K and 600 RPM

**Fig. 7.16.** Modeled nitric acid concentration profile for the dissolution of 
(U\textsubscript{0.78}Pu\textsubscript{0.22})O\textsubscript{2} MOX pellet in 8 M HNO\textsubscript{3} at 348 K and 600 RPM
Fig. 7.17. Modelled plutonium concentration profile for the dissolution of 
$(U_{0.78}Pu_{0.22})O_2$ MOX pellet in 8 M HNO$_3$ at 348 K and 600 RPM

From the data given in Table 7.2, the activation energy for all the processes was calculated using Arrhenius equation and they were found to be about 31.7, 21.5, 26.6 and 17.5 kJ/mol for the processes with the rate constants $k_P$, $k_h$, $k_c$ and $k_{Pu}$ respectively in the temperature range 343-373 K.

7.7.2.1.2. Case II: Neglecting the autocatalytic effect of uranyl ion in solution

If autocatalytic effect of uranyl ion is not considered, then equation (7.4) need not be considered for deriving the rate equations. In that case, the rate equation gets modified as follows.

\[
\frac{dW_{ue}}{dt} = -k_p [HNO_3] W_{ue} \quad (7.12)
\]

\[
\frac{dW_e}{dt} = k_p [HNO_3] W_{ue} - \left( k_h [HNO_3]^2 + k_{Pu} [HNO_3]^2 \right) W_e \quad (7.13)
\]

\[
\frac{d[\text{UO}_2^{2+}]}{dt} = (MV)^{-1} \left( k_h [HNO_3]^2 \right) W_e \quad (7.14)
\]

\[
\frac{d[\text{Pu}^{4+}]}{dt} = (MV)^{-1} \left( k_{Pu} [HNO_3]^2 \right) W_e \quad (7.15)
\]

\[
\frac{d[HNO_3]}{dt} = -\left( MV \right)^{-1} \left( 3k_h [HNO_3]^2 + 4k_{Pu} [HNO_3]^2 \right) W_e \quad (7.16)
\]
The experimental data of concentrations of nitric acid, uranium and plutonium as a function of time were fitted into above rate equations using a nonlinear regression technique to obtain the rate constant that best correlates the experimental data. The best values were obtained by minimizing the following objective function

$$f = \sum_{i=1}^{n} 20 \left( C_{U\text{exp}} - C_{U\text{calc}} \right)^2 + \sum_{i=1}^{n} \left( C_{\text{HNO}_3\text{exp}} - C_{\text{HNO}_3\text{calc}} \right)^2 + \sum_{i=1}^{n} 20 \left( C_{\text{Puexp}} - C_{\text{Pucalc}} \right)^2$$  \hspace{1cm} (6.17)

The rate constants $k_p$, $k_h$ and $k_{Pu}$ were calculated at different conditions of temperature and acidity. The values of rate constants and corresponding standard deviation are tabulated in tables 7.4 and 7.5.

**Table 7.4. Rate constants for the dissolution of MOX fuel at different temperatures**

<table>
<thead>
<tr>
<th>T(K)</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_p$ ([L/mol]/min)</td>
<td>4.12E-04</td>
<td>5.25E-04</td>
<td>6.32E-04</td>
<td>7.02E-04</td>
</tr>
<tr>
<td>$k_h$ ([L/mol]/min)</td>
<td>4.60E-05</td>
<td>6.21E-05</td>
<td>7.35E-05</td>
<td>8.30E-05</td>
</tr>
<tr>
<td>$k_{Pu}$ ([L/mol]/min)</td>
<td>1.11E-05</td>
<td>1.29E-05</td>
<td>1.68E-05</td>
<td>1.88E-05</td>
</tr>
<tr>
<td>sd(U)</td>
<td>0.027</td>
<td>0.0278</td>
<td>0.0311</td>
<td>0.0293</td>
</tr>
<tr>
<td>sd(HNO$_3$)</td>
<td>0.1114</td>
<td>0.1059</td>
<td>0.134</td>
<td>0.1267</td>
</tr>
<tr>
<td>sd(Pu)</td>
<td>0.0082</td>
<td>0.0123</td>
<td>0.0108</td>
<td>0.0104</td>
</tr>
</tbody>
</table>

**Table 7.5. Rate constants for MOX fuel dissolution at different acidity**

<table>
<thead>
<tr>
<th>[HNO$_3$] (M)</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>11.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_p$ ([L/mol]/min)</td>
<td>5.87E-04</td>
<td>5.17E-04</td>
<td>4.89E-04</td>
<td>5.38E-04</td>
</tr>
<tr>
<td>$k_h$ ([L/mol]/min)</td>
<td>1.02E-04</td>
<td>6.32E-05</td>
<td>4.23E-05</td>
<td>4.05E-05</td>
</tr>
<tr>
<td>$k_{Pu}$ ([L/mol]/min)</td>
<td>1.35E-05</td>
<td>1.32E-05</td>
<td>1.02E-05</td>
<td>1.02E-05</td>
</tr>
<tr>
<td>sd(U)</td>
<td>0.0294</td>
<td>0.0277</td>
<td>0.0208</td>
<td>0.0235</td>
</tr>
<tr>
<td>sd(HNO$_3$)</td>
<td>0.1248</td>
<td>0.1059</td>
<td>0.0997</td>
<td>0.1277</td>
</tr>
<tr>
<td>sd(Pu)</td>
<td>0.0037</td>
<td>0.0124</td>
<td>0.0046</td>
<td>0.0053</td>
</tr>
</tbody>
</table>
The concentration profiles of uranium, nitric acid and plutonium during the course of dissolution were determined using the model equations 7.12 to 7.16. The comparison between experimental and calculated values of [U(VI)], [HNO$_3$] and [Pu$^{4+}$] vs time at 353 K are shown as semi log plots in Figures 7.18 to 7.20 respectively. Similar plots were also generated for each of the conditions mentioned in the tables 7.4 and 7.5.

**Fig. 7.18.** Modelled uranium concentration profile for the dissolution of $(U_{0.78}Pu_{0.22})_2$O$_2$ MOX pellet in 8 M HNO$_3$ at 353 K and 600 RPM

![Uranium Concentration Profile](image1)

**Fig. 7.19.** Modelled nitric acid concentration profile for the dissolution of $(U_{0.78}Pu_{0.22})_2$O$_2$ MOX pellet in 8 M HNO$_3$ at 353 K and 600 RPM

![Nitric Acid Concentration Profile](image2)
Fig. 7.20. Modelled plutonium concentration profile for the dissolution of 
\((\text{U}_{0.78}\text{Pu}_{0.22})\text{O}_2\) MOX pellet in 8 M HNO$_3$ at 353 K and 600 RPM

From the data given in Table 7.4, the activation energy for all the processes was calculated using Arrhenius equation and they were found to be about 19.1, 20.7 and 19.6 kJ/mol for rate constant $k_p$, $k_h$ and $k_{pu}$ respectively in the temperature range 343-373 K.

During the dissolution of MOX pellets, it is only uranium which undergoes oxidative dissolution, whereas, plutonium remains in the same oxidation state both in the solid and liquid. Also, as uranium being more than 70% in mass and they have formed a perfect solid solution, the overall dissolution profile is sigmoidal due to the autocatalytic nature of urania dissolution in presence of nitrous acid. Figures 7.15 and 7.18 are the predicted uranium profiles with and without autocatalytic effect. Both the predicted profiles are fairly accurate indicating the insignificance of the catalytic effect of uranyl ion. In fact the predicted uranium profiles match the experimental values more closely in the absence of the catalytic effect of uranyl ion. This further emphasizes the absence of any catalytic action of uranyl ion. Whereas when it comes to predicting the plutonium profiles, shown in figures 7.17 and 7.20, neglecting the catalytic effect of uranyl ion markedly improves the prediction. This clearly shows that uranyl ion doesn’t catalyze the dissolution of plutonia.
7.7.2.2. **Method 2: Considering non-ideal nature of particle during the reaction**

**7.7.2.2.1. Introduction**

Similar to the data analysis carried out for the dissolution of UO$_2$ pellets in section 5.10.V, the experimental data of the U, Pu MOX dissolution experiments were also analyzed considering the non-ideal nature of the particle during the reaction for the determinations of its kinetics.

**7.7.2.2.2. Model equations**

The shrinking particle model was invoked by including the interaction of chemical reaction and diffusion together. Model equations were derived in the same way as that of UO$_2$ and urania ceria MOX pellet dissolution. As this is a MOX pellet, while deriving the rate equation, the reaction of ceria with nitric acid also needs to be considered. Due to the presence of plutonium as an additional species here, we will be ending up with three rate equations unlike in the case of UO$_2$ (where it was only 2), i.e. one each for predicting the concentration profile of nitric acid, uranyl ion and ceric ion in the solution as a function of time. In this derivation, the subscript ‘A’, ‘B’ and ‘E’ were used respectively to denote nitric acid, uranyl ion and plutonyl ion respectively. Here also the accessible surface area was taken into account and is denoted by A. It is calculated as per equation 5.88 given in the section 5.10.c.v in the previous chapter. The surface area (A) and the subscript ‘A’ denoting nitric acid ($X_A$) are differentiated sufficiently all through the derivation. As the derivations are already explained in detail in section 5.10 of this thesis, the same is not repeated here. The final rate equations for determining the concentration profiles of various species are given in the following equations.

For nitric acid, \[
\frac{dC_A}{dt} = (v_{AB}k_B C_{LA}^s + v_{AE}k_E C_{LA}^s) \cdot A
\] (7.18)

For uranium, \[
\frac{dC_B}{dt} = v_B k_B C_{LA}^s \cdot A
\] (7.19)

For plutonium, \[
\frac{dC_E}{dt} = v_E k_E C_{LA}^s \cdot A
\] (7.20)

The values for the stoichiometric coefficients used are $v_{AB} = 2.75$, $v_{AE} = 4$, $v_B = v_E = 1$. 

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The rate constants were estimated at different temperatures. Comparison between experimental and calculated values of the concentration profiles of uranyl ion, ceric ion and bulk phase nitric acid were generated graphically as a function of time and are shown in the figures in the following section for various conditions as the cases may be. The temperature dependency of the dissolution rate is governed by the Arrhenius equation. Thus the plot of ln (k) vs 1/T gives a slope equal to (-Ea/R) from which the apparent activation energy of the dissolution reaction under the experimental conditions were estimated. The best values of the rate constants were obtained by minimizing the objective function given in the following equation.

\[ f = \sum_{1}^{n} 20 \left[ \left( C_{B\text{exp}} - C_{B\text{calc}} \right)^2 \right] + \sum_{1}^{n} 50 \left[ \left( C_{A\text{bexp}} - C_{A\text{bcalc}} \right)^2 \right] + \sum_{1}^{n} 50 \left[ \left( C_{E\text{exp}} - C_{E\text{calc}} \right)^2 \right] \]  

(7.21)

The comparison between the experimental and calculated concentration profiles using the model equations were given graphically in the following sections for various cases.

The above model equations are applied for all the experimental data generated to study the effect of initial concentration of nitric acid, mixing rate (RPM) and temperature. For each of the above experiment, model equations were used to determine the rate constants for two different situations namely the order with respect to nitric acid being 1 and 2.

7.7.2.2.1. Case 1: Order w.r.t. nitric acid is 1

The comparison between the experimental and the predicted concentration profiles of nitric acid, uranium and plutonium for the dissolution of U_{0.78}Pu_{0.22}O_2 MOX pellets in 8 M nitric acid at 353 K, assuming order w.r.t. to nitric acid is unity were shown in Figures 7.21 to 7.23.
Fig. 7.21. Comparison of experimental and calculated profiles of [U(VI)] at 353 K for \( U_{0.78}Pu_{0.22}O_2 \) MOX pellet dissolution assuming 1st order w.r.t. HNO\(_3\).

Fig. 7.22. Comparison of experimental and calculated 1st order [HNO\(_3\)] profiles at 353 K for \( U_{0.78}Pu_{0.22}O_2 \) MOX pellet dissolution.
Fig. 7.23. Comparison of experimental and calculated profiles of [Ce(IV)] at 353 K for \( U_{0.78}Ce_{0.22}O_2 \) MOX pellet dissolution assuming 1\(^{st}\) order w.r.t. HNO\(_3\)

![Graph of Ce(IV) profile comparison](image)

7.7.2.2.2. Case 2: Order w.r.t. nitric acid is 2

Figures 7.24 to 7.26 shows the comparison between the experimental and the predicted concentration profiles of nitric acid, uranium and cerium for the dissolution of \( U_{0.78}Ce_{0.22}O_2 \) MOX pellets in 8 M nitric acid at 353 K with the assumption that the order w.r.t. to nitric acid is two. The experimental data only up to 60% of the dissolution was considered for modeling as beyond that the pellets crumbled and the value of the shape factor is no more a constant and changes very drastically.

Fig. 7.24. Comparison of experimental and calculated profiles of [U(VI)] at 353 K for \( U_{0.78}Ce_{0.22}O_2 \) MOX pellet dissolution assuming 2\(^{nd}\) order w.r.t. HNO\(_3\)

![Graph of U(VI) profile comparison](image)
7.7.3 Conclusion on the modeling of simulated U, Pu MOX pellet dissolution

The modeling of the experimental data on the dissolution of urania plutonia MOX pellets in nitric acid under various conditions of acidity, temperature and mixing rate were carried out in two different methods, viz. penetration based and surface area based methods, very similar to that for UO$_2$ and urania ceria MOX pellets dissolution mentioned in the Chapters 5 and 6 respectively.
The model predictions were presented in section 7.7.2 which shows that the prediction of the concentration profiles to be fairly accurate in both the methods. In the case of plutonium profiles predicted by the penetration method (section 7.7.2.1), the predicted profile was always higher than the actual when the catalytic effect of uranyl ion is considered\(^5\). But when the catalytic effect of uranyl ion is neglected, the accuracy of the predicted profiles improved substantially, especially in the case of plutonium. This suggests that the uranyl ion does not play any catalytic role during the dissolution process. This is the reason for the reduced accuracy of the model equations in method 1 when the catalytic effect of uranyl ion was considered.

When it comes to the surface area based method, the accuracy of the model equations (equations 7.18 to 7.20) in predicting the concentration profiles of uranium, nitric acid and plutonium was found to be very good similar to the case of UO\(_2\) and urania ceria MOX pellets dissolution studies. This is because, the experimental concentration profiles and the starting area of the pellet before dissolution are the input required for this method and since these parameters are fairly accurate, the method was found to be satisfactory. Ambiguity could arise only in the case of urania plutonia MOX pellet dissolution studies due to the lack of a suitable analytical equipment to measure the pellet surface area resulting in some errors. Since the pellets used for the studies were dimensionally rejected due to surface chippings, the actual area would be higher than that calculated from the pellet dimensions. It could also be noted that the predicted concentration profiles are almost the same irrespective of the order of the reaction with respect to nitric acid being 1 or 2. To sum up on the modeling of the urania-plutonia dissolution behaviour in nitric acid, it could be understood that both the methods used here describes the reaction fairly well. But if one has to employ them for the realistic dissolution of spent fuel pellets, which would be more porous due to the gaseous fission products generated inside the pellet matrix, the former method (penetration based) would be superior. This is due to the difficulty in measuring the starting surface area of these highly radioactive pellets which is the starting data required for the second method (surface area based).

Finally it could be concluded based on the findings of the current work presented in Chapters five to seven that the experiments carried out as a part of this research thesis has generated the fundamental model equations required to predict the dissolution behaviour of a typical plutonium rich MOX nuclear fuel under PUREX process conditions. The
findings reported in this thesis would also pave way for planning and carrying out more work in the future for studying the dissolution behaviour of irradiated fuel samples. This would enable development of more accurate dissolution models and also would serve as a launching pad for understanding the dissolution process of irradiated nuclear fuel.

7.8 Post justification of using cerium as a surrogate of plutonium in its MOX dissolution studies

The experimental results of Chapter six and seven clearly indicate that the behaviour of simulated MOX pellets and the urania plutonia MOX pellets under similar conditions are comparable qualitatively. The faster dissolution rates of these two types of fuel pellets when compared to urania pellets under similar conditions may be attributed to different reasons. In the case of urania ceria MOX pellets, the fast dissolution rate was due to the fabrication procedure wherein the solids where formed directly from the homogenous solution leading to better solid solution formation during sintering. In the case of urania plutonia MOX pellets, though the fabrication method was the same as that of the urania pellets, their densities were slightly lesser and also they had an annular hole in their centre which provided more area of contact between the pellet and acid. Therefore they dissolved rapidly than their urania counterpart under similar conditions. Based on all these experimental observations, it could be inferred and henceforth justify cerium as a good non-radioactive surrogate for plutonium under the conditions that prevailed during the dissolution experiments.

7.9 Overall rate equation for the nuclear fuel dissolution process

The dissolution model equations for the MOX pellets were developed by employing two different methods, namely penetration and surface area based. The calculated concentration profiles are found to be more accurate in the case of penetration method than in the surface area based method. This is because; the penetration method is based on the weight measurements which were done more accurately. But in the case of surface area based method, due to the lack of a suitable facility to measure the surface area of the dissolving pellet containing plutonium, they were arrived based on the initial surface area measurement from the pellet dimensions. It should be recollected at this point that all the fuel pellets employed in this study were dimensionally rejected since they had minor defects in the form of end chipping. This leads to higher surface area of the pellets that are
not accounted for when the surface area of the pellet was calculated from its dimensions assuming ideal geometry. Therefore it could be concluded from the current work that the model equations based on the penetration method given in equations 7.12 to 7.16 correlates to the experimental values better. In the future when equipments were made available for the accurate measurement of surface area for radioactive pellets, the surface area based dissolution model equations give in equations 7.18 to 7.20 would also predict the dissolution behaviour of MOX pellets more accurately.

7.10 References

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4 Shabbir, M.; Robbins, R. G. Kinetics of the dissolution of uranium dioxide in nitric acid. I. J. Appl. Chem. 1968, 18, 139–134