CHAPTER 2. Spent nuclear fuel reprocessing

2.1. Why reprocessing?
For any fuel to make a significant impact in the energy scenario, its sustainability should be ensured. The sustainability of the nuclear fuel depends not only on the effectiveness of operating the reactor with the desired fuel but also on how far the fuel could be burnt completely. For this, unburnt material from the spent fuel has to be recovered for recycling back. Hence the aim of any nuclear fuel reprocessing plant should be to remove the fission products (and its associated radioactivities) quantitatively from the spent fuel and recover the plutonium and uranium in them to the purest extent possible. This would enable tapping of more energy from the given amount of fuel. From the Indian standpoint, the closed nuclear fuel cycle is the most preferred and advisable option for nurturing nuclear power in meeting the long term energy security of the country. This is because of the limited uranium reserve in the country. Additionally, if we have to devise a strategy to deploy our huge thorium reserve, this could be the best option. Hence reprocessing is a mandatory option for us. Reprocessing the spent fuel offers various other advantages as listed below.

1. By reprocessing and reusing the recovered fissile materials in breeder reactors, we are multiplying the amount of energy that could be extracted from the given quantity of fuel. Hence this leads to the conservation of natural resources
2. Nuclear fuel reprocessing is the precursor to the recovery of actinides from the spent fuel. Hence reprocessing paves way for better management of nuclear waste. Also the removal of long lived actinides (like $^{241}$Am, $^{237}$Np etc.) from the spent fuel leads to minimization of environmental impact of the radioactive waste
3. When the recovered fissile materials are reused, it strengthens fuel cycle economics
4. As reprocessing recovers all the fissile materials from it, especially plutonium, they could be directed for peaceful applications, thereby taking care of proliferation resistance

2.2. Nature of spent nuclear fuel
Nuclear fuels are generally of three types, namely, metallic, ceramic and dispersion. The latter includes two-phase metallic fuels such as Al-UAl$_3$ as well as dispersions of ceramics in metal or ceramic matrices. Irrespective of the chemical form of the nuclear fuel, the
irradiated/spent nuclear fuel will always be comprised of the unburnt initial fuel which is the bulk, fission products whose mass number ranges from about 70 to 160 and the minor actinides (mostly comprising of Am, Np and Cm). Depending on the burn up of the fuel, the composition of all these vary vastly. Depending on the type of fuel, the chemical form of the fission products and minor actinides also differ. The composition of the spent fuel depends on how long the fuel was in the reactor (burnup) and to a greater extent on how long the irradiated fuel has been out of the reactor. This amount of time for which the irradiated fuel is kept outside the reactor, with all the appropriate safety measures, from the time of its discharge till its further management in the nuclear fuel cycle is called the ex-vessel cooling period. For a light water reactor (like a PWR or BWR) the $^{235}\text{U}$ levels get reduced from the initial amount by about 2-4%. The change is even lower for CANDU type reactors (less than 1%). About 95% of the spent fuel is still $^{238}\text{U}$, which could be used again. The other radionuclides that now exist in the irradiated fuel are heavy elements and their isotopes (plutonium, americium, neptunium and curium) and fission products. Although there are thousands of tons of spent fuel, it is compact and uniform. This makes it relatively easy to manage this waste. The typical composition of the spent fuel discharged from a commercial light water reactor is given in Table 2.1.

**Table 2.1. Typical composition of the spent fuel from a commercial LWR**

<table>
<thead>
<tr>
<th>Element or group</th>
<th>Percent, by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>95.6%</td>
</tr>
<tr>
<td>Plutonium</td>
<td>0.9%</td>
</tr>
<tr>
<td>Fission products</td>
<td>3%</td>
</tr>
<tr>
<td>Heat emitters line $^{137}\text{Cs}$ and $^{90}\text{Sr}$</td>
<td>0.3%</td>
</tr>
<tr>
<td>Minor actinides</td>
<td>0.1%</td>
</tr>
<tr>
<td>Transmutable $^{131}\text{I}$ and $^{99}\text{Tc}$</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

2.3. Choice of reprocessing process

Depending on the chemical form of the nuclear fuel, the method of reprocessing the spent nuclear fuel is chosen. Basically there are two primary means of reprocessing the spent nuclear fuel. They are the aqueous and non-aqueous methods. In the former, nitric acid medium is used for dissolving the spent fuel either with or without their cladding material. Once all the fuel material in brought into a suitable medium, they are separated from the
host of fission products and their associated radioactivity by solvent extraction process. In the latter method, a variety of non-aqueous methods like pyrometalurgical process, halide volatility process, carbo-chlorination process, direct electrochemical dissolution process etc. are available. Since the current thesis focusses only on the dissolution of spent nuclear fuel in aqueous medium, methods associated to aqueous processes are only discussed here. For oxides, nitrides and carbides, the aqueous based methods could be adopted. The well-known PUREX process comes under this category. For metallic fuels, as they are seldom soluble in aqueous based solvents, hence non-aqueous methods like pyrometalurgical and pyrochemical processes are employed.

2.4. Chemistry of the reprocessing of spent nuclear fuel by PUREX process
The subject of the present thesis is the dissolution kinetics of nuclear fuel in nitric acid medium. Hence information/discussion presented in the thesis would pertain to this aspect alone. However, a brief mention about the other processes also would be made in the thesis. The following is a brief account of the chemistry involved in the various process steps while processing a spent nuclear fuel by aqueous methods.

The process flowsheet for reprocessing of spent fuel by aqueous process (PUREX process in particular) could be divided into three sections namely the head-end, solvent extraction and tail-end process sections. The head-end processes comprises of dismantling the subassemblies (SAs) into individual pins in case of FBR fuel reprocessing or individual SAs in the case of thermal reactor fuel reprocessing, chopping them into small pieces of suitable size and dissolving them in nitric acid. The process chemistry comes into the picture only from the dissolution step as the spent fuel is converted to a suitable physical and chemical form for efficient downstream processes only in this step. The tail-end process refers to the conversion of the purified plutonium and uranium nitrates to their respective solid oxides which are the final products of a nuclear fuel reprocessing plant. Fig. 2.1 depicts the typical processes carried out in the reprocessing of spent nuclear fuel by PUREX process.

2.4.1. Chemistry in the head-end steps in the PUREX process
The head-end processes involve decladding, dissolution and feed filtration and conditioning. The chemistry involved in these processes is described in the following sections.
2.4.1.1. Chemistry involved in the decladding of nuclear fuel

Decladding refers to the pretreatment given to the spent fuel to ensure direct access for the aqueous solvent to the fuel material for further processing. Decladding could be carried out either by chemical methods or by mechanical means. In chemical decladding, preferential dissolution of cladding material is carried out with a suitable reagent, leaving the fuel undissolved. Subsequently, the fuel is dissolved in nitric acid. For example, aluminium cladded uranium oxide spent fuel is decladed with caustic solution which dissolves aluminium as per the following reaction \(^{16}\).

\[
\text{Al} + 0.85 \text{NaOH} + 1.05 \text{NaNO}_3 \rightarrow \text{NaAlO}_2 + 0.9 \text{NaNO}_2 + 0.15 \text{NH}_3 + 0.2\text{H}_2\text{O} \quad (2.1)
\]

The fuel does not dissolve in sodium hydroxide. There are processes to dissolve Zr and stainless steel clads as well. But they are not generally practiced in plant scale. While chemical decladding eliminates the use of mechanical system in radioactive areas, it increases the waste volume by introducing new chemical species in the process streams. Even though the chemical decladding procedure is followed in some plants for reprocessing the spent fuel from research reactors, chop-leach process is the widely followed process to expose the fuel to nitric acid in dissolution leaving the clad “undissolved” so that it could be handled separately. This enables cladding hulls to be compacted and disposed-off as high level solid waste separately.

Chopping is carried out in mechanical chopping equipment. Generally bundle chopping
procedure is followed for the thermal reactor fuel reprocessing plants while for FBR fuel reprocessing plants, single pin chopping is adopted. This avoids crimping of the chopped bits due to the slenderness of the fuel pins, which reduces the fuel dissolution rates.

2.4.1.2. Chemistry involved in the dissolution of nuclear fuel

The dissolution step in the PUREX process primarily aims at the following tasks\(^\text{17}\):

i. Complete transfer of the fissile materials (U and Pu) into the aqueous solution

ii. Complete separation of the fuel from the cladding material

iii. Render feasibility for the accurate measurement of the amounts of fissile material taken for reprocessing for the purpose of nuclear material accounting and

iv. Convert the entire spent fuel into an appropriate chemical form amenable for their subsequent separation and quantitative recovery.

In the PUREX process, the fuel is dissolved in boiling nitric acid. Generally 6-8 M nitric acid would be adequate for most of the spent fuels of PHWRs, but plutonium rich fuels require still higher acidities\(^\text{18}\).

Dissolution of FBR fuels with plutonium greater than 35% by weight in an oxide matrix is difficult with concentrated nitric acid alone.\(^\text{19}\) Higher plutonium concentration invariably demands advanced dissolution methods like addition of strong oxidizing/reducing agents or by electrolysis. When the reprocessing of a mixed carbide fast reactor spent fuel (FRSF) was taken up for the first time in the world at CORAL\(^\dagger\), Kalpakkam, it was believed that a 70% plutonium rich FRSF cannot be dissolved in pure nitric acid. But the CORAL operating experience has revealed that reflux heating in boiling concentrated nitric acid could dissolve it completely.\(^\text{20}\)

Though, most of results in the published literature\(^\text{21, 22, 23, 24, 25, 26, 27}\) were inconclusive in recommending a specific condition for dissolving spent fuel on a commercial scale, they still provided certain important inferences, which helped in providing direction for the subsequent research, some of which are as follows.

i. Initial dissolution rates depends on concentration of nitric acid and temperature\(^\text{28}\)

ii. Similar to UO\textsubscript{2}, plutonium lean spent fuels could be dissolved in nitric acid\(^\text{29}\)

iii. Spent fuel with plutonium content above 35% by weight of the total heavy metal

\(^\dagger\) CORAL stands for the COmpact Reprocessing of Advanced fuels in Lead shielded facility which is set-up at IGCAR, Kalpakkam, India for demonstrating the feasibility of reprocessing the plutonium rich spent fuel discharged from FBTR. CORAL was formerly known as the Lead Mini Cell (LMC).
needs aggressive conditions for dissolution

iv. Irradiation renders the fuel more brittle commensurate with the burnup of the fuel due to the gaseous fission products, decay heat and neutron flux. Therefore when agitated physically, small fragments of fuel particles is released out of the chopped fuel pin into the acid medium, which dissolve faster than those inside the chopped pin. Additionally, due to the escape of such small particles from the inside the chopped fuel pin pieces, more space is available for ingress of acid. This enhances the dissolution of the fuel particles still intact inside the chopped fuel pin pieces. Thus irradiation enhances dissolution rate.

v. Irradiation also leads to the formation of certain alloys in the spent fuel comprising of the noble metals (Ru, Rh, Pd) and actinides leading to undissolved residues. This leads to the loss of some fissile materials in these alloys. The amount of actinides, plutonium in particular, present in these undissolvable alloys increases with burnup.

vi. Voloxidation in general enhances dissolution, but also increases the amount of plutonium left in the undissolved residue.

Owing to the above facts, there has been more attention on the dissolution of high plutonium bearing spent fuel, especially those discharged from a fast reactor. The additional issue of criticality due to the presence of high amount of plutonium in these types of fuel makes it more challenging to develop the process for dissolution.

Until the end of the 20th century, the necessity for developing superior dissolution methods for the spent nuclear fuel and scraps, stemmed predominantly from nuclear waste management. Only in the recent decade owing to plutonium utilization strategies, reprocessing of plutonium containing fuels has taken the center stage wherein dissolution of spent fuel has been an integral part. In the early 1960s, Uriarte and Rainey came out with the recommendations for commercially dissolving irradiated MOX fuel. According to them, nitric acid with traces of HF was the most suitable medium for the dissolution of MOX fuel. But subsequently based on the studies to eliminate corrosive reagents like HF, a method based on cerium(IV) was developed. It was proposed that this method not only is devoid of a corrosive reagent but also enhances plutonium oxide dissolution. Also it was found to be superior to other strong oxidants, including ozone, permanganate, persulphate and Ce(IV). During dissolution, Ce(IV) gets reduced to Ce(III) which needs to be re-oxidized in-situ. The main disadvantage of this method is the increased consumption of Ce(IV) by the other oxidizable fission products like Ru.
In 1980, Ryan and Bray\textsuperscript{35} of PNL gave an account of the problem of dissolving plutonium oxide from a thermodynamic and kinetics standpoint. These studies showed that thermodynamically it is impossible to dissolve pure PuO\textsubscript{2} in nitric acid solutions of concentration below about 4 M. Fluoride ion was used based on its ability to complex Pu(IV) in strong acidic solutions, wherein it aids in increasing both the solubility and the rate of PuO\textsubscript{2} dissolution. The formation of the Pu(IV) fluoride complex influences the dissolution process. Hence the fluoride concentration often must exceed the final dissolved plutonium concentration. In irradiated MOX fuels, many scraps and various plutonium contaminated waste, other contaminants such as Si, Zr, U, and various fission products also form fluoride complexes. They virtually prevent the dissolution of PuO\textsubscript{2} when present in large quantity unless a large excess of fluoride is used. Processes for leaching plutonium from various scraps have often employed repeated cycles of leaching by fluoride containing nitric acid solutions. Not only has this produced large volumes of solutions, generating eventually more waste, but significant amounts of Al\textsuperscript{3+} are generally added to the solutions (further increasing waste) to complex the fluoride, both to allow normal plutonium processing by ion exchange or solvent extraction and to minimize fluoride corrosion of equipment. When silica or silicates are present, the volatilization of SiF\textsubscript{4} could produce significant problems in off-gas systems, and silica often precipitates when Al is added to prepare the solution for further processing.

Ryan et.al\textsuperscript{36}, as a follow up to the above findings, proposed a process to dissolve PuO\textsubscript{2} and PuO\textsubscript{2}\textsuperscript{2+} ions by using electrical energy and it was named CEPOD (Catalyzed Electrolytic Plutonium Oxide Dissolution). In this process, PuO\textsubscript{2} is dissolved in an analyte containing small (catalytic) amounts of elements that form kinetically fast, strongly oxidizing ions. The oxidizing ions are regenerated at the anode; they act in a catalytic manner, carrying electrons from the solid PuO\textsubscript{2} surface to the anode of the electrochemical cell.

Among the various methods employed in the studies to enhance the dissolution of spent fuel in nitric acid, voloxidation was expected to be a prominent technique.\textsuperscript{37} The studies revealed that voloxidation though enhances dissolution and leaves more plutonium in the undissolved residues which are even harder to dissolve.

\textit{2.4.1.2.1. Dissolution reactions}

Various reactions taking place during the dissolution of different types of nuclear fuel materials are summarized in the following few sections.
2.4.1.2.1.1. **Dissolution of uranium metal**

\[ \text{U} + 6\text{HNO}_3 \rightarrow \text{UO}_2(\text{NO}_3)_2 + 3\text{NO}_2 + \text{NO} + 3\text{H}_2\text{O} \quad (2.2) \]

2.4.1.2.1.2. **Dissolution of plutonium metal (in the presence of HF)**

\[ \text{Pu} + 6\text{HNO}_3 \rightarrow \text{Pu}(\text{NO}_3)_4 + \text{NO}_2 + \text{NO} + 3\text{H}_2\text{O} \quad (2.3) \]

\[ \text{Pu} + 6\text{HNO}_3 \rightarrow \text{PuO}_2(\text{NO}_3)_2 + 3\text{NO}_2 + \text{NO} + 3\text{H}_2\text{O} \quad (2.4) \]

\[ \text{Pu} + 6\text{HNO}_3 + 2\text{H}^+ \rightarrow \text{Pu}(\text{NO}_3)_3 + 2\text{NO}_2 + \text{NO} + 4\text{H}_2\text{O} \quad (2.5) \]

2.4.1.2.1.3. **Dissolution of UO\(_2\) with emission of NO\(_x\) gases**

\[ \text{UO}_2 + 4\text{HNO}_3 \rightarrow \text{UO}_2(\text{NO}_3)_2 + 2\text{NO} + 2\text{H}_2\text{O} \quad (2.6) \]

\[ 3\text{UO}_2 + 8\text{HNO}_3 \rightarrow 3\text{UO}_2(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O} \quad (2.7) \]

\[ 2\text{UO}_2 + 6\text{HNO}_3 \rightarrow 2\text{UO}_2(\text{NO}_3)_2 + \text{NO} + \text{NO}_2 + 3\text{H}_2\text{O} \quad (2.8) \]

During the dissolution of UO\(_2\), depending on the concentration of the nitric acid, one or more of the above reaction take place. The reaction corresponding to equation 2.6 occurs when the concentration of nitric acid is above 8M. As the acid concentration reduces, the reaction proceeds predominantly through reaction 2.7 and when the acidity reduces below 6M, reaction 2.8 predominates. Though the stoichiometric equations are well established, the detailed mechanism of the reaction has not been completely understood. Though, some of studies in the literature had speculated the role of intermediates like nitrous acid getting generated in-situ during the dissolution process\(^{38, 39, 40}\), no studies have yet been carried out systematically to quantify the role of nitrous acid during dissolution. Hence the present work aims at studying these reactions in detail by determining the quantitative effect of various influencing parameters like initial concentration of nitric acid, temperature, mixing intensity, role of nitrous acid and the surface area of the pellet.

2.4.1.2.1.4. **Dissolution of PuO\(_2\) with emission of NO\(_x\) gases**

Unlike UO\(_2\), PuO\(_2\) dissolves in nitric acid very sluggishly\(^ {16}\) as per the following stoichiometric equations.

\[ \text{PuO}_2 + 4\text{HNO}_3 \rightarrow \text{PuO}_2(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O} \quad (2.9) \]
PuO\(_2\) + 6HNO\(_3\) → PuO\(_2\)(NO\(_3\))\(_2\) + 3NO\(_2\) + NO + 3H\(_2\)O \hspace{1cm} (2.10)
PuO\(_2\) + 8HNO\(_3\) → PuO\(_2\)(NO\(_3\))\(_2\) + 6NO\(_2\) + 4H\(_2\)O + O\(_2\) \hspace{1cm} (2.11)
PuO\(_2\) + 4H\(^+\) → Pu\(^{4+}\) + 2 H\(_2\)O \hspace{1cm} (2.12)
PuO\(_2\) + NO\(_3^-\) + 2H\(^+\) → PuO\(_2^{+}\) + NO\(_2\) + H\(_2\)O \hspace{1cm} (2.13)
PuO\(_2\) + NO\(_3^-\) + 3H\(^+\) → PuO\(_2^{2+}\) + HNO\(_2\) + H\(_2\)O \hspace{1cm} (2.14)

All the above reactions require high concentration of nitric acid at elevated temperatures for quantitative dissolution of plutonia. Generally higher the concentration of the acid used the off-gas NO\(_X\) will be dominated by NO\(_2\). Otherwise it is NO. The reaction 2.12 represents the direct dissolution of PuO\(_2\) in nitric acid whereas equations 2.13 and 2.14 represent the oxidative dissolution of PuO\(_2\). Thermodynamic calculations presented in the literature have shown that all the above dissolution reactions of PuO\(_2\) in nitric acid are thermodynamically less favorable\(^{34,41}\).

2.4.1.2.1.5. Dissolution of UC, PuC and their mixture

Uranium, plutonium and their mixed carbides are known to dissolve even under mild conditions as compared to their oxide counterparts\(^{42}\) with the emission of CO\(_2\) and NO\(_X\) gases as per the following reactions.

UC + 6HNO\(_3\) → UO\(_2\)(NO\(_3\))\(_2\) + CO\(_2\) + 3NO + NO\(_2\) + 3H\(_2\)O \hspace{1cm} (2.15)
PuC + 8HNO\(_3\) → Pu(NO\(_3\))\(_4\) + CO\(_2\) + 2NO + 2NO\(_2\) + 4H\(_2\)O \hspace{1cm} (2.16)

The earliest studies carried out for the direct dissolution of advanced carbide fuels in nitric acid medium showed the formation of some organics like oxalic and mellitic acids\(^{43}\). In addition to these, some more unidentified compounds were also reported\(^{44}\). All these organics generated during the dissolution process were expected to have adverse effect on the subsequent purification of uranium and plutonium by solvent extraction using tributyl phosphate (TBP).

2.4.1.2.2. Kinetics, mechanism and modeling of dissolution

Many proposals were brought forward to explain the kinetics and mechanism of dissolution as and when the existing knowledge on the dissolution of spent fuel is being updated by the researchers world over. Some of these proposals were followed by
mathematical modeling for explaining the experimental observations. Lot of work was carried out to study the kinetics, mechanism and modeling of dissolution of uranium and plutonium oxides in nitric acid for the development of a continuous dissolution equipment and process methodology. Understandably UO$_2$ dissolution mechanism was studied first which paved way for the evaluation of the reaction mechanism of the dissolution of other actinide oxides. Detailed discussions of literature information on this aspect are presented in Chapter 3 of this thesis.

2.4.1.3. Chemistry of the dissolver off-gas treatment

The dissolver off-gases are cooled and the NO$_X$ gases evolved during the dissolution are scrubbed in DM/distilled water and converted to nitric acid. This is done primarily for two purposes, namely, to reduce the release of NO$_X$ gas into atmosphere and also to minimize the overall consumption of nitric acid during reprocessing by recycling this acid to an appropriate stage within the reprocessing process. The following reactions occur during the dissolver off-gas treatment:

2.4.1.3.1. Gas phase reactions

\[
\begin{align*}
2\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \\
2\text{NO}_2 & \rightarrow \text{N}_2\text{O}_4 \\
\text{NO} + \text{NO}_2 & \rightarrow \text{N}_2\text{O}_3
\end{align*}
\] (2.17-2.19)

2.4.1.3.2. Liquid phase reactions

\[
\begin{align*}
2\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{HNO}_3 + \text{HNO}_2 \\
\text{N}_2\text{O}_4 + \text{H}_2\text{O} & \rightarrow \text{HNO}_3 + \text{HNO}_2 \\
\text{N}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_2 \\
3\text{HNO}_2 & \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}
\end{align*}
\] (2.20-2.23)

It could be seen that oxygen is required for conversion reactions which is supplied by sparging air$^{16}$. Oxygen in air enhances the conversion of NO to NO$_2$ which has better absorption characteristics with water. The off-gases are then treated for the removal of iodine and then filtered through High Efficiency Particulate Air (HEPA) filters and discharged into the environment through the stack after making sure that the radioactivity of the off-gas stream is within the limits stipulated by the regulatory authority$^{45}$.
2.4.1.4. Decladding chemistry

Decladding is carried out to avoid the clad to be present along with the fuel in further processing since its presence makes the process design very complicated. During the spent nuclear fuel processing by aqueous processes, the cladding material of the fuel would be removed by either of two different ways, viz, mechanical or chemical. The conventional PUREX process removes the clad by mechanical means wherein during the dissolution step, the fuel material inside the chopped fuel pins alone goes into the solution leaving the clad materials undissolved. This undissolved clad after dissolution is termed as the “HULL” and is disposed as solid radioactive waste after appropriate treatment. The chemical decladding process is adopted in those cases wherein the fuel material is bonded with the clad material as in the case of uranium metal slugs bonded with aluminium-silicon alloy to aluminium could during the early production reactions in the US. As the clad and fuel are bonded, mechanical decladding is not feasible here. In the chemical decladding process, the clad materials alone will be dissolved in a alkali leaving out the spent fuel which does not dissolve in that. Then the left over fuel material will be removed and dissolved in nitric acid medium for further processing. The THOREX process adopted for reprocessing the thorium based spent nuclear fuel employs this method wherein the cladding material is Aluminium. Thus an appropriate decladding method is adopted suitably to avoid the cladding materials being present along with the fuel materials during solvent extraction process. In earlier days when the mechanical decladding process was not developed, the chemical decladding process was used in the zirflex and sulfex processes for removing the zircaloy and SS clad materials respectively.

2.4.1.5. Chemistry of feed clarification

Under boiling nitric acid condition, all the fuel material dissolves leaving a small quantity of fine residues which mainly consists of noble metal alloys with small quantities of plutonium in it. Though the quantity of this undissolved material depends upon the nature of the fuel, burnup and initial plutonium content, it generally increases with the burnup and plutonium composition. Typically this quantity could be as high as 0.74% in FBR fuels. The dissolver solution is filtered to remove these fine particles before subjecting it to solvent extraction. The filtration also removes the clad fines. Though R&D work was conducted with sand bed as well as bag filters, centrifuge filters are more commonly used.
2.4.2. Chemistry involved in feed conditioning

Feed conditioning is the process step carried out to ensure that the chemical conditions of the dissolver solution, viz, acidity and valency of the metal ions of interest, is adjusted for getting the highest possible recovery of uranium and plutonium in an optimum number of extraction stages. While generally 1-3 M is the optimum range of acid concentration employed in the processing of PHWR spent fuels, 4-6 M is used for fast reactor fuels as its plutonium content is higher. This is because the extraction coefficient of plutonium is relatively lower at lower acidities. This range of acid concentration was found to be optimum for the quantitative recovery of both uranium and plutonium as well as for removing bulk of the fission products whose extraction is poor under these conditions. For ensuring quantitative recovery, all the plutonium is converted to its fourth valency state, as the distribution coefficient of Pu(IV) ($D_{Pu(IV)}$) is the highest among all the plutonium species under PUREX process conditions. Since plutonium co-exists in III, IV and VI oxidation states in nitric acid medium, it is essential to convert all the plutonium species to Pu(IV). It is also well established that Pu(IV) undergoes disproportionation in nitric acid medium by which it gets converted to III and VI valency states partially. Though the kinetics of disproportionation is found to be reasonably slow under PUREX process conditions, it is a general practice to carry out conditioning of the feed solution just before carrying out solvent extraction. Valency adjustment of plutonium could be carried out either chemically or electrolytically.

2.4.2.1. Conditioning by chemical methods

Sparging with NO$_2$ gas is the most commonly practiced chemical method for conditioning the feed in the PUREX process. The earlier practice of using NaNO$_2$ for insitu generation of NO$_2$ for conditioning has been dispensed with in most of the recent plants since this would increase the solid waste quantities by introducing Na$^+$ ions in the liquid waste streams. NO$_2$ gas, when sparged into aqueous solution, produces nitrous acid in-situ by the following reaction.

$$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$$ (2.24)

The nitrous acid (HNO$_2$ or NO$_2^-$) generated in-situ in the solution converts all plutonium species in the dissolver solution to Pu(IV) by the following equations.
Though the most stable oxidation state of uranium in nitric acid medium is VI, presence of any hydrazine (used in its nitrate form as a stabilizing agent of U(IV) in the latter stages of PUREX process) may lead to the reduction of U(VI) to U(IV). The nitrous acid produced in-situ, also takes care of this issue as per the following reaction:\(^{59}\)

\[
\begin{align*}
N_2H_4 + 2HNO_2 &\rightarrow N_2 + N_2O + 3H_2O \quad (2.28) \\
N_2H_5NO_3 + HNO_2 &\rightarrow HN_3 + 2H_2O + HNO_3 \quad (2.29) \\
HN_3 + HNO_2 &\rightarrow N_2 + N_2O + H_2O \quad (2.30)
\end{align*}
\]

The above reactions takes very rapidly\(^\textit{60}\) and destroy hydrazine ions completely in the system thereby avoiding the reduction of U(VI) to U(IV).

### 2.4.2.2. Conditioning by electrochemical methods

Alternately, the PUREX process feed conditioning could also be carried out electrochemically using platinum as anode and titanium as cathode. The electrochemical reactions that take place during such an electrochemical conditioning is given by

\[
\begin{align*}
Pu^{3+} &\rightarrow Pu^{4+} + e^- \quad E = -0.914V \quad (2.28) \\
Pu^{6+} + 2e^- &\rightarrow Pu^{4+} \quad E = 1.054V \quad (2.29)
\end{align*}
\]

Though studies have shown that electrolytic conditioning is possible\(^\textit{61}\), this has not been introduced in any of the plants till date. Most probably this could be due to some of the parasitic electrochemical reactions which could take place simultaneously leading to some undesired changes in the conditioned feed and also in excess consumption of power\(^\textit{62}\). The valency of uranium need not be adjusted as its VI valency is the most stable state and hence it remains so by default. The equilibrium acid concentration has a strong effect on the solvent extraction efficiency as shown in Fig. 2.2.
From Fig. 2.2 it could be seen that the D values for U(VI) and Pu(IV) is sufficiently high above 4 M acid concentration when compared with that of the fission products, lanthanides and other actinides. Hence the solvent extraction step is carried out using 30% TBP after conditioning the feed acid concentration to above 4 M during FBR spent fuel reprocessing for achieving the required decontamination for uranium and plutonium from the rest of the species in the spent fuel. Since the FBR spent fuel has higher quantity of Pu, the PUREX process is normally operated with the concentration of nitric acid at or above 4 M. When the spent fuel is short cooled, the concentration of acid is maintained even at 6 M for the first cycle alone to have sufficient decontamination factor (DF) from Ru. Though $^{95}$Zr has a short half-life of only about 65 days, there will be sufficient amount of it in FBR spent fuel due to the higher burn up. Hence for the decontamination of Zr(IV) whose distribution is sufficiently high at above 4 M acid concentration, a acid scrub of about 3-3.5 M is provided for the loaded organic to strip the extracted Zr(IV), if any.

2.4.3. Chemistry of solvent extraction process

The Organisation for Economic Co-operation and Development (OECD), Nuclear Energy Agency (NEA) has come out with a report prepared by an expert committee in 2012 which is one of the latest compilations as on date on the solvent extraction relevant to spent fuel
reprocessing and recovery of actinides and lanthanides from the high level liquid waste\textsuperscript{64}. The conditioned feed solution would then be subjected to solvent extraction using 30\% TBP diluted in n-dodecane as solvent for the quantitative recovery of U(VI) and Pu(IV) in the first cycle of solvent extraction. The stoichiometric equation for the extraction of uranium and plutonium by TBP is given in the following equations.

\begin{align}
\text{UO}_2^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{TBP}(\text{org}) & \rightarrow \text{UO}_2(\text{NO}_3)_2.2\text{TBP}(\text{org}) \quad (2.30) \\
\text{Pu}^{4+}(\text{aq}) + 4\text{NO}_3^-(\text{aq}) + 2\text{TBP}(\text{org}) & \rightarrow \text{Pu}(\text{NO}_3)_4.2\text{TBP}(\text{org}) \quad (2.31)
\end{align}

After extraction of U(VI) and Pu(IV) into the organic phase, the loaded organic is separated and contacted with a fresh dilute nitric acid stream. As the Fig. 2.2 indicates, the distribution coefficient of U(VI) and Pu(IV) is lower when the concentration of acid in the aqueous stream in contact with it is less. Hence they get stripped back to the aqueous phase. Pu(IV) is prone for polymerization when the concentration of the acid is low\textsuperscript{65}. Since the recovery of the polymerized Pu(IV) is very difficult, care needs to be exercised in choosing the concentration of the strip acid to ensure the prevention of plutonium polymerization. This operation of extraction and stripping is termed as \textbf{one cycle of solvent extraction}. Sufficient numbers of such cycles of solvent extraction is carried out during reprocessing to achieve the required levels of decontamination for the final uranium and plutonium products from all the fission products and other impurities.

\section*{2.4.4. Chemistry of U/Pu partitioning in the PUREX process}

The uranium and plutonium, after being purified from the bulk of fission products and other impurities, is separated from each other in the next cycle which is called the partitioning cycle. The relatively lower distribution co-efficient of Pu(III) into 30\% TBP is exploited advantageously for this purpose. As mentioned earlier in section 2.4.2.1, hydrazine stabilized U(IV)\textsuperscript{66} is the commonly used reducing agent for this purpose. U(IV) reduces all Pu(IV) to Pu(III) as per the following reaction\textsuperscript{67}.

\[ 2\text{Pu(IV)} + \text{U(IV)} \rightarrow 2\text{Pu(III)} + \text{U(VI)} \quad (2.32) \]

Thus for every mole of Pu(IV), half the mole of U(IV) is sufficient for effecting the
reduction. Depending on the fuel composition, partitioning could be carried out either in the organic or in the aqueous phase. When the plutonium composition in the spent fuel is relatively low like that in PHWR (typically 0.3 weight %), organic phase partitioning is preferred. In this case, the 1st cycle loaded organic product containing U(VI) and Pu(IV) is contacted with an aqueous scrub stream containing excess amount of hydrazine stabilized U(IV). This U(IV) gets extracted into the loaded organic and it reduces Pu(IV) to Pu(III). In real practice it was found that the quantity of U(IV) required is much higher than the stoichiometry due to various reasons like poor extractability of U(IV), presence of nitrous acid and absence of hydrazine in the organic phase to stabilize U(IV) etc. Since Pu(III) has a very low distribution co-efficient, it immediately strips into the aqueous phase. Thus the loaded organic would retain all the U(VI) and all Pu(III) would strip into the aqueous stream thereby effecting the partitioning.

In the case of FBR spent fuel reprocessing wherein plutonium concentration is higher (typically 20-30 weight %), carrying out partitioning in the organic phase after co-extraction of both uranium and plutonium would lead to unduly higher load of uranium on the plant as very high amount of U(IV) would be required to reduce all plutonium quantitatively in the organic phase. This is because of the combined effects of lower distribution co-efficient of U(IV) in TBP and many side reactions which consumes hydrazine thereby leading to oxidation of U(IV) to some extent in nitric acid medium. Hence while processing plutonium rich spent nuclear fuel, aqueous phase partitioning would be more economical from the overall plant capacity point of view. In aqueous phase partitioning, during the conditioning of the 1st cycle strip product, hydrazine stabilizeduranous is added marginally more than the stoichiometric requirement (about 10% in excess) to convert all plutonium to Pu(III). Subsequently when this conditioned feed solution is subjected to solvent extraction, as Pu(III) has a poor distribution co-efficient in TBP, only U(VI) gets extracted leaving out Pu(III) and the excess U(IV) in the aqueous feed itself. The extracted U(VI) is then stripped using dilute nitric acid which is the partitioned uranium product stream. The Pu(III) left in the aqueous feed which is referred to as the partitioned plutonium product stream, had undergone one cycle of solvent extraction lesser when compared to the uranium stream. Hence it requires more purification from fission products and other associated impurities.

The U(IV) which is the reducing agent used in the partitioning cycle may be added externally or may be generated in-situ by electrolysis. The former method refers to the
chemical partitioning cycle and the latter is referred as the electrolytic/electrochemical partitioning.

2.4.5. Chemistry of the uranium purification cycle

The partitioned uranium product stream may contain some traces of plutonium and fission products which need to be further purified. This is done by solvent extraction using 30% TBP in n-dodecane as the solvent to obtain the purified uranyl nitrate solution (UNS). Depending on the levels of plutonium concentration, hydrazine stabilized uranous is also used to get the required decontamination from plutonium to enable the qualifying of final U₃O₈ product to be handled in fume hood type of containment. The UNS is then taken for reconversion operations for converting them to U₃O₈ through precipitation.

2.4.6. Chemistry of the plutonium purification cycle

The partitioned plutonium product stream depending on whether the partitioning is carried out by organic or aqueous phase partitioning will have certain amount of fission products as contaminants. In the case of aqueous phase partitioning since the plutonium stream is subjected to one cycle of solvent extraction lesser as compared to its uranium counterpart, the plutonium stream will be relative more contaminated with the fission products. Therefore it is taken to the plutonium purification cycles for further decontamination from fission products by employing a 20% TBP solution as the solvent to obtain the purified plutonium nitrate solution (PNS). When the amount of plutonium in the spent fuel is as high as in the case of FBRs, the plutonium purification cycles becomes more essential for not just purifying the plutonium product stream, but also to deliver a concentrated purified plutonium feed to the plutonium reconversion (PuRC) lab. This helps especially in two important ways. One is by making the PuRC feed concentrated and hence the % loss of plutonium during precipitation is reduced and secondly in reducing the work load of the laboratory personnel by reducing the volume of feed to be processed and thereby also leading to a reduction in the manrem expenditure.

The first step in this cycle is to condition the feed with respect to plutonium valency as plutonium is present in its third valency in the partitioned plutonium product stream. This is carried out similar to the feed conditioning step explained in section 2.4.2. The product stream obtained at the end of the plutonium purification cycle is the PNS which would be
sent to the plutonium reconversion lab to obtain the final PuO₂ product.

2.4.7. Chemistry of the tail-end processes during reprocessing

The uranium and plutonium reconversion operations wherein the purified nitrate solutions of uranium and plutonium are converted to their respective solid oxide products through precipitation process is referred to as the tail-end processes in a spent nuclear fuel reprocessing plant.

2.4.12.1. Chemistry of plutonium reconversion operation

In the plutonium reconversion section, the feed PNS is conditioned to a concentration of 3.5 M nitric acid ensuring all the plutonium to be present in their +4 valency for quantitative precipitation. Oxalic acid is the precipitant used which is mixed with the conditioned feed in a definite proportion to precipitate all plutonium as Pu(IV) oxalate hexahydrate quantitatively. The reaction takes place as per the following equation.

\[
\text{Pu(NO}_3\text{)}_4 + 2\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}_2\text{O} \rightarrow \text{Pu(C}_2\text{O}_4\text{)}_2.6\text{H}_2\text{O} \downarrow + 4\text{HNO}_3
\]  

The plutonium oxalate precipitate obtained is then filtered, dried and calcined to obtain the final PuO₂ product. The reactions taking place during calcination are given below.

\[
\text{Pu(C}_2\text{O}_4\text{)}_2.6\text{H}_2\text{O} \rightarrow \text{Pu(C}_2\text{O}_4\text{)}_2 + 6\text{H}_2\text{O} \tag{2.34}
\]

\[
\text{Pu(C}_2\text{O}_4\text{)}_2 + \text{O}_2 \rightarrow \text{Pu(CO}_3\text{)}_2 + 2\text{CO}_2 \tag{2.35}
\]

\[
\text{Pu(CO}_3\text{)}_2 \rightarrow \text{PuO}_2 + 2\text{CO}_2 \tag{2.36}
\]

The rate of addition of feed, precipitant, intensity of mixing and temperature of the reaction mixture plays an important role in deciding the physical properties of the precipitate obtained.

2.4.12.2. Chemistry of the uranium reconversion operation

In the uranium reconversion operation, the UNS received from the uranium purification cycle is taken for precipitation of uranium as ammonium diuranate (ADU) by using liquid ammonia as the precipitant. The precipitation reaction takes place as per the following stoichiometric equation.
The ADU precipitate is then filtered, dried and calcined to get the final oxide product which is a mixture of UO₃ and UO₂. The reactions taking place during calcination are given in the following equations.

\[(\text{NH}_4)_2\text{U}_2\text{O}_7 \rightarrow 2\text{UO}_3 + 2\text{NH}_3 + \text{H}_2\text{O} \quad (2.38)\]
\[(\text{NH}_4)_2\text{U}_2\text{O}_7 + 2\text{H}_2 \rightarrow 2\text{UO}_2 + 2\text{NH}_3 + 3\text{H}_2\text{O} \quad (2.39)\]

In reprocessing plants, the calcination of ADU to obtain uranium oxide is normally carried out at about 773 K in the presence of air. Hence it is the reaction 2.38 which takes place predominantly. Thus the final oxide product obtained is a mixture of UO₃ and UO₂ which is normally referred as U₃O₈ (2UO₃ + UO₂).

### 2.5. Options for the dissolution of spent nuclear fuel in aqueous media

The primary purpose of the dissolution process step during the reprocessing of the spent nuclear fuel is to convert the spent fuel material to a suitable chemical and physical form that enables easy recovery of the fissile material present in them in the downstream process steps. As liquid is the most preferred physical form for the ease of its handling, dissolution aims at converting the spent fuel into their liquid form.

Among the various techniques available for separation of the species of our interest from a whole lot of material as is the case of spent nuclear fuel reprocessing wherein uranium and plutonium are separated from all the fission products practically comprising of all the elements in the periodic table, solvent extraction is the most preferred technique. This is because the technique is simple and amenable for commercial scale engineering with remote operations.⁷⁰

The next choice to be made is for the medium of dissolution. The oxide form of the nuclear fuel materials are ceramic and are generally known to be chemically inert. Hence to dissolve them we need strong mineral acids. The choices in that sense are limited to hydrochloric acid, nitric acid, and Sulphuric acid. Though there are processes like

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* ADU – Ammonium diuranate is a compound of variable composition and is sometimes expressed as NH₄(UO₃)₂·3H₂O or as UO₂(OH)ₓ·xH₂O·yNH₃ where x and y depend on production conditions.
Sulfex\textsuperscript{71} and Darex\textsuperscript{72} wherein Sulphuric and aquarea were used respectively during the dissolution either for chemical decladding or the dissolution itself, these processes have their own problems in terms of the stability of the resulting actinide sulphates or the corrosive nature of the solvent in the case of chlorides\textsuperscript{73}. It was also found that TBP does not selectively extract actinides as their chlorides\textsuperscript{74}. One of the main reasons for not employing sulphuric acid as the medium of dissolvent in nuclear fuel reprocessing is the fact that UO\textsubscript{2} has poor solubility in it and also the inextractability of U(VI) sulphates by TBP\textsuperscript{75, 76}. Similarly HF could not be used because of the insolubility of UF\textsubscript{4}. Thus nitric acid turns out to be the most preferred mineral acid for the dissolution of oxide nuclear fuel materials during its reprocessing.

2.6. Importance of studying UO\textsubscript{2} and MOX dissolution kinetics
The INPP is presently in the beginning of the second of its three stages wherein FBRs are going to be the predominant nuclear power producing reactors. As emphasized earlier in this thesis, the success of FBR program is very much dependent on how efficiently and quickly its spent fuel is reprocessed and put back into the reactor for power production. As MOX is going to be the driver fuel at least for the initial FBRs, it is important to study their behavior during reprocessing particularly its dissolution in nitric acid. By understanding the dissolution behavior of these fuel materials in nitric acid, one could get deeper insight into their dissolution kinetics which is the basic input data required for designing the continuous dissolution system for this fuel. For the commercial scale reprocessing of these fuel materials, it is desirable to have continuous process systems as they reduce the overall inventory of the fuel materials outside the reactor in the entire nuclear fuel cycle. This would auger well for the safety of the processing and also would help in having better control over the nuclear material accounting. The continuous dissolution system also increases the overall plant capacity in addition to shrinking the floor space occupancy of the plant in comparison to batch mode of operation.

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