

**THORIA / THORIA-URANIA DISSOLUTION STUDIES FOR
REPROCESSING APPLICATION**

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GOVERNMENT OF INDIA
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Thoria/Thoria-Urania Dissolution Studies for Reprocessing Application

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1. Abstract

Thoria dissolution is normally conducted in 13M nitric acid in the presence of 0.03M sodium fluoride or HF as catalyst and 0.1M aluminium nitrate for mitigation of fluoride related corrosion of SS 304L dissolver vessel. Addition of aluminium nitrate in such high concentrations has undesirable consequences in the downstream high level radioactive liquid waste vitrification process at 900-1000°C. Besides, because of the highly corrosive nature of fluoride ion, lowering its concentration in the dissolution reaction is advantageous in reducing the corrosion of dissolver and other downstream equipments. The present work was done with twin objectives of avoiding aluminium nitrate addition and lowering the fluoride ion concentration during dissolution reaction. High temperature sintered thoria and thoria-4 weight% urania dissolution reactions were investigated in the absence of aluminium nitrate and at reduced fluoride concentrations. Corrosion rates of SS 304L and zircaloy in various dissolvent mixtures were studied by weight loss method. These studies clearly showed that aluminium nitrate addition for control of fluoride related corrosion of SS 304L can be avoided when zircaloy-clad thoria/thoria-urania pellets are dissolved. Dissolved zirconium ion was observed to be as effective as aluminium ion. Moreover, dissolution could be achieved with reasonable reaction rates at reduced fluoride concentration of 0.005-0.01M instead of 0.03M by changing the method of addition of the fluoride catalyst.

2. Introduction

In view of vast resources of thorium in our country, its utilization has been identified as a key element in our country's nuclear energy programme to meet the long time energy security. Our country has envisaged three stage nuclear energy power programme. In the first phase, natural uranium based fuel is being used in the presently operating PHWR type power reactors. Plutonium produced in these

reactors by nuclear reactions as a byproduct will be used in fast breeder reactors in the second stage of our programme.. In these reactors, thorium is used as a blanket material which produces U^{233} as a result of nuclear reactions. Th along with U^{233} or Pu is the fuel considered for the third phase of Nuclear Energy Power Program. This is expected to give nuclear power for many more years to come.

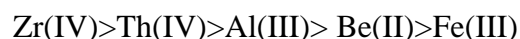
The difficulties faced in the thorium fuel cycle are mainly in the reprocessing domain. Dissolution of highly refractory thoria, is one of the difficult steps in the spent thoria fuel reprocessing. One of the reasons for this difficulty is because of the non-variable oxidation state of thorium, i.e., Th(IV), which obviously closes options of oxidative-reductive dissolution like in other ceramic oxides (mainly U and Pu). The dissolution of thoria in pure nitric acid is very slow and incomplete; extent of dissolution being quite low for sintered thoria. Thermodynamic parameters are unfavourable and, therefore, addition of highly reactive fluoride ion appears to be inevitable to accomplish the dissolution of thoria by fluoride complexation equilibria to shift the thermodynamics into favourable region and achieving effective dissolution of thoria. Mechanism of thoria dissolution in the presence of fluoride ion is governed by the formation of surface fluoride complexes. These surface complexes react with protons and fluoride ions in the aqueous medium in a rate controlling reaction [1, 2].

Standard Thorex dissolvent consisting of concentrated nitric acid containing 0.03M sodium fluoride and 0.1M aluminium nitrate has been used in our engineering scale campaigns for dissolution of research reactor irradiated aluminium-clad Thoria after chemical decladding using aqueous NaOH. Presence of fluoride ions in nitric acid dissolution process enhances the corrosion of dissolver vessel made of SS 304L [3]. To control the corrosion, $Al(NO_3)_3$ is usually added. Aluminium ion forms complex with free fluoride ions present in the solution and thereby reduces the corrosion of SS.

Presence of aluminium ion at such high concentrations (0.1M) leads to undesirable consequences in the downstream vitrification process adopted for management of high level radioactive waste. Waste loading in the glass reduces to about 13% from the normal value of about 20%. This will result in undesirable increase in the volume of vitrified waste product. Besides, glass melt viscosity increases and foaming problems also arise during vitirification operations. Therefore,

it is advantageous to avoid or minimize the use of aluminium ion during thoria dissolution.

It is known that fluoride ion forms strong complexes not only with aluminium but also with zirconium, thorium ions etc. The strength of the 1:1 complexes in decreasing order is as follows [1]:



Stability constants for the simple fluoride complexes (MF) with some of these metal ions is shown in the table-1 [3, 4].

Table-1: Stability constants of simple fluoride complexes (MF)

Complexing Metal Ion	Log. Stability constant
H^+	3.1
Al^{3+}	7.0
Th^{4+}	8.6
Zr^{4+}	9.8

It is evident from table-1 that zirconium and thorium ions form stronger complexes with fluoride ion than aluminium ion. Zircaloy will be used as a clad material for power reactor thoria based nuclear fuels. In the presence of fluoride ion, zirconium in the clad material dissolves, to some extent, in the nitric acid medium. Dissolved zirconium ion can complex with free fluoride more effectively than aluminium ion and inhibit corrosion. Besides, thorium ion concentration also builds up in the dissolvent solution as the thoria dissolution reaction progresses. As seen above, thorium ion also forms stronger complex with fluoride ions and can inhibit corrosion. It means that in the zircaloy-clad thoria dissolution reaction, zirconium ions and thorium ions exist in nitric acid to control corrosion of SS dissolver vessel. It was, therefore, felt that addition of aluminium nitrate may not be required to mitigate the corrosion. A detailed experimental study was done to verify this assumption. Dissolution reaction was also studied at reduced fluoride concentrations. This would reduce the corrosion of downstream equipments and associated off-gas systems.

Results of these studies showed that aluminium nitrate addition is not necessary and fluoride concentration can be reduced to 0.005 -0.01M.

3. Materials and Methods

High temperature sintered thoria and 96 weight%thoria-4% urania pellets (referred to as MOX pellets here in after) were procured from RMD, BARC and used in the experiments. Sintering temperature was about 1700°C. Density of the pellets varied from 8.0-10.0g/cc. Typical dimensions of the cylindrical thoria pellet were 17mm length, 12 mm diameter; *weight was ~17g* while that of MOX pellet was 7-8 grams. Dimensions of the cylindrical MOX pellet were 10 mm diameter and 10 mm length. Cylindrical zircaloy-2 clad tube of dimensions 14 mm OD and 23 to 16 mm length was used. It was procured from MSD and AFD, BARC for the experiments. Other chemicals used were of AR grade and used as received. Sodium fluoride was used as catalyst in all the experiments. Plain, polished SS 304 L coupons having surface area 15-26 cm² were used in the experiments for corrosion study.

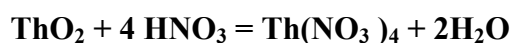
The study was restricted to dissolution in 13M nitric acid with varying concentrations of sodium fluoride. Dissolution was carried out in 250 ml borosilicate glass flasks fitted with water-cooled reflux condenser to minimize the loss of dissolvent by evaporation. One single thoria pellet or **two** MOX pellets at a time were used for the experiments. The reaction mixture was about 50-60 ml in most experiments. The reaction mixture was heated to boiling temperature under total reflux using electrotheramal mantle. *The ratio of the volume of 13M nitric acid to the weight of thoria/MOX pellet was maintained at nearly 4.0 unless otherwise stated.* At this ratio, the acid concentration and thorium ion concentration at the end of the dissolution reaction will be about 9.5M and one molar respectively. Feed adjustment for the downstream THOREX solvent extraction process can be simply done by water dilution. It does not require acid killing step for THOREX feed adjustment. Appropriate quantities of NaF in 1M aqueous stock solution form were added to 13M nitric acid to maintain the desired fluoride concentration in the dissolvent. Initial boiling temperature of the reaction was observed to be about 110°C. This would gradually decrease as the nitric acid concentration decreases to less than 10.0M.

In order to monitor the progress of the dissolution reaction, solution samples were drawn at regular intervals. **Since the reaction time was more than 24 hours in most of the experiments, the sampling interval was conveniently kept 24 hours.** Thorium content in the sample was estimated titrimetrically with EDTA reagent using xylenol orange indicator. In many experiments, the residual thoria weight was also measured at the end of the experiment after washing and drying besides titrimetric analysis for estimation of thorium ion. **Since the percentage dissolution after a certain reaction period varied 5 to 10 % during repetitive experimental runs, the % dissolution was expressed in the form of range while reporting the results.**

In order to study the corrosion of SS 304L and zircaloy-2, polished coupon of SS 304L along with cylindrical tube of zircaloy-2 were placed in the dissolvent mixture during the dissolution experiment. In order to simulate the plant conditions more closely, zircaloy tube was used as envelope around the oxide pellet in some of the later experiments and dissolution reaction kinetics was studied. In experiments on MOX, two pellets were enclosed in one zircaloy clad tube. To study the corrosion rate of SS and dissolved concentration of zirconium, pre-weighed coupons of SS 304L and Zircaloy-2 tubes of known dimensions were added to the dissolvent before starting the experiment. After the dissolution reaction, these metal samples were washed, dried and weighed for finding the weight loss. Corrosion rate of SS coupon was expressed in mpy. Dissolved zirconium concentration was calculated and expressed as g/l or in molarity.

4. Results & Discussion

Thoria dissolution in nitric acid can be represented by the following reaction:



In the absence of fluoride ion in the reaction mixture, the dissolution reaction did not progress to any significant extent even after 45 hours. This is in agreement with the literature information. It is reported that dissolution of thoria in the absence of fluoride is very low, being $1.5 \text{ E-}06 \text{ mmole/min-cm}^2$ [5]. Mechanism of thoria dissolution in nitric acid in the presence of fluoride was discussed in Shying's papers [1,2]. In his mechanistic study, he proposed adsorption of fluoride ion onto the active sites of thoria surface resulting in complex formation. These surface sites were

proposed to be decomposed hydroxyl groups. The concentration of these active sites on thoria surface depends on the method of preparation, particularly heat treatment of the oxide. This postulation explains the pronounced effect of history of preparation on such surface reactions. It is for this reason that in many previous studies reported, powdered, rather than massive thoria pellets were employed in experiments to ensure better reproducibility. Reaction of aqueous fluoride and hydrogen ions with these surface complexes leads to dissolution of thoria. This step is rate controlling. Shying's study has indicated that the dissolution of thoria in nitric acid /fluoride system involves the following steps:

- Surface hydroxyl formation by reaction between the oxide and water or protonated species
- Dissociation of these surface compounds in acid solution to provide a positively charged surface species
- Fluoride adsorption and formation of surface complex
- Reaction of protons and aqueous fluoride with the fluorinated surface sites in a rate-controlled reaction
- Decomposition of thorium fluoride complex accompanied by thoria dissolution

Results obtained on thoria/MOX dissolution kinetics at different fluoride concentrations and corrosion data were presented in the following sections of the report.

4.1 Dissolution studies at 0.03M fluoride concentration

Results of the experiments with standard thoria dissolvent consisting of 13M nitric acid and 0.03M sodium fluoride in the presence of 0.1M aluminium nitrate and zircaloy were shown in table-2:

Table-2: Sintered Thoria pellet dissolution reaction in 13M nitric acid in **the presence of 0.03M sodium fluoride and 0.1M aluminium nitrate and zircaloy** under boiling and reflux conditions

Run No.	Reaction Time (Hours) For				SS 304L corrosion rate (mpy)	Zirconium concentration in dissolvent (g/l)
	80-85% dissolution	85-90% dissolution	90-95% dissolution	95-100% dissolution		
1*	5 hour sampling showed 53% dissolution and SS corrosion of 161 mpy			24	44	Not applicable
2**	5 hour sampling showed 33% dissolution	24	40	72	12	Not applicable
3	24	48		72	5	1.8
4	27	45		71	14	1.83
5	24	48		72	13	4.2
6	24	35	53	72	6	4.9

*Zircaloy and aluminium nitrate were not added in the reaction mixture;

**Zircaloy was not added in the reaction mixture

Note: Sampling interval in all the experiments reported in this study was 24 hours unless otherwise stated

Results of table-2 show that near quantitative dissolution of thoria has occurred in all the experimental runs at 0.03M fluoride concentration. In the experimental run no.1 in the table-2, aluminium salt and zircaloy addition was intentionally avoided to see the effect on corrosion rate and kinetics. The reaction, in the absence of zircaloy and aluminium salt, completed in just 24 hours. In this reaction, the only fluoride complexing metal ion is thorium whose concentration has increased from zero to about one molar in 24 hours. As anticipated, the initial rate of thoria dissolution was high with 53% dissolution in five hours. However, it took 24 hours for the completion of the reaction. This could be on account of the increased extent of fluoride complexation by thorium ions. Other factors such as decrease in available thoria pellet surface area, nitric acid concentration and temperature with the progress of the reaction are also responsible for the decrease in the rate of the

reaction. The reaction is kinetically controlled with an apparent activation energy of 19 kcal/mole at 0.03M fluoride concentration. The initial dissolution rate expression was reported to be as follows [6]:

$$-\frac{d}{dt} [\text{ThO}_2] = k [\text{HNO}_3] [\text{HF}]^{0.5}$$

Initial Corrosion rate of SS 304L coupon in the run no. 1 was very high, being 161 mpy. This could be attributed to the following factors: Fluoride ion in the reaction mixture can participate in the three following competitive reactions:

- 1) It can get adsorbed on the active sites of thoria surface and form surface complex
- 2) It can complex with metal ions such as thorium, zirconium, aluminium etc. in the aqueous phase. Equilibrium concentration of fluoride in the solution is expected to change with time and depends on factors such as concentration of each metal ion, concentration of acid, thoria pellet surface area. Therefore, it is a complex system of multiple reactions
- 3) Fluoride can react with metallic surfaces such as SS and zircaloy resulting in their corrosion. This, in turn, depends on the thermodynamic and kinetic aspects of these reactions.

In the early stages of the reaction in run no.1, there is no fluoride-complexing metal ion in the aqueous solution. That could be the reason for the high initial corrosion rate of SS. As the reaction progressed, thorium ion accumulation in the aqueous phase reduced the corrosion of SS to 44 mpy at the end of the reaction. If this is the case, it would be advantageous to employ only very small portion of fluoride at the beginning of the reaction to build up some initial concentration of thorium ions before maintaining the desired level.

In run no. 2, 0.1M aluminium nitrate was added to see the change in the kinetics and, especially, the corrosion rate of SS. Corrosion rate expectedly reduced from 44 to 12 mpy on account of the complex formation of fluoride with aluminium ion initially and subsequently with thorium ion also. Formation of aluminium fluoride complex right in the early stages might have led to the decrease in the kinetics of the thoria dissolution reaction. In the first 5 hours, the extent of dissolution was 33% (ca. 53% in the run no. 1). The reaction completion time increased by three

fold, from 24 to 72 hours. In the subsequent runs in table-2, zircaloy was also present along with aluminium salt. The reaction time did not increase and continued to be about 72 hours. Presence of zirconium ion besides aluminium and thorium ions should have reduced the rate of dissolution which was not the case. Fluoride ion must have preferentially complexed with the dissolving zirconium ion from zircaloy clad instead of aluminium ion. In that case, presence of aluminium salt appears to be of no consequence. Zirconium concentration after the completion of reaction was observed to vary from 1.8-4.9 g/l (0.02-0.05M) in these runs. As shown in table-1, zirconium and thorium ions form stronger complexes with fluoride than aluminium ion. Corrosion rate varied from 5-14 mpy in different experiments. Reasons for the variation in the corrosion rates of zircaloy and SS are not entirely clear. However, it could be due to some changes in the surface characteristics of thoria pellets in different experiments which affect the aqueous fluoride adsorption. The number of active sites on the thoria surface determines the extent of fluoride adsorption from solution. If the fluoride adsorption is more initially, the corrosion of SS and Zr in the early stages of the reaction will be less.

Zirconium and thorium ions, as said earlier, form stronger complexes with fluoride compared to aluminium ion. Therefore, it was felt that addition of aluminium nitrate for corrosion mitigation may be unnecessary. In the next series of experiments, thoria dissolution experiments were conducted *in the presence of zircaloy without addition of aluminium nitrate*. Results of these experiments were shown in table-3 below:

Table-3: Sintered Thoria pellet dissolution reaction in 13M nitric acid in **the presence of 0.03M sodium fluoride and zircaloy** under boiling and reflux conditions: *Al salt concentration: Nil*

Run No.	Reaction Time (Hours) For			SS 304L corrosion rate (mpy)	Zirconium concentration in dissolvent(g/l)	Remarks
	85-90% dissolution	90-95% dissolution	95-100% dissolution			
7	24		48	6.5	1.3	NaF was added all at once in the beginning of the reaction
8	24		47	10	1.4	In the first five hours, NaF was 0.01M; after 5 hours, increased to 0.03M in the solution
9		24	47	11.5	1.8	---do---
10		48	72	7.7	2.8	Pellet was enclosed in zircaloy tube; split addition of fluoride was used; pellet density:9.43 g/cc. 80-85% dissolution was observed in 24 hours.
11	24	48	72	7.8	2.1	--do--; pellet density: 9.38 g/cc

Table-3 clearly shows that the absence of aluminium nitrate in the dissolvent did not increase the corrosion rate of SS 304L. Corrosion rate in the present system is in the range of 6.5-11.5 mpy (ca. 5-14 mpy-table 2). Therefore, it is clear that zirconium dissolving from zircaloy clad along with thorium ion was able to control the corrosion of SS 304L even in the absence of aluminium salt. It is attributed to the strong complexing ability of zirconium ion with fluoride ion, as shown in table-1. Zirconium ion concentration at the end of the reaction was observed to be 1.3-1.8 g/l(0.014-0.02M). Initial zirconium ion concentration in the dissolvent is zero. The biphasic reaction between aqueous fluoride and solid zircaloy results in the generation of aqueous zirconium ion. It is significant to note that the heterogeneous nature of fluoride ion reaction with zircaloy did not lead to excessive corrosion of SS 304L, presumably due to more favourable free energy changes. Considering this biphasic reaction aspect, fluoride addition into the dissolvent was done in two installments, initially maintained at lower 0.01M and with time gap of 5 hours (referred to as split addition hereinafter) restored to 0.03M in all the experimental runs except the first

one of table-3. Though there was not much difference in the nature of results in this experimental system, this split addition was found to have beneficial effects at lower fluoride concentrations as shown in the subsequent discussion. In the experiments where envelope of zircaloy clad was used around the pellet (run nos. 10&11), the reaction times increased, due to limited surface availability, from 47-48 to 72 hours. Results presented in table-3 clearly showed that ***addition of aluminium nitrate is not necessary during zircaloy clad thoria dissolution.***

Experimental results obtained for MOX pellets containing 96% thoria and 4% UO₂ by weight are reported in table-4. ***Aluminium nitrate addition was avoided in all the subsequent experiments on the basis of results obtained for thoria.***

Table-4: MOX dissolution reaction in 13M nitric acid in the presence of 0.03M sodium fluoride under boiling and reflux conditions: MOX pellet (2 nos.) weight: 14.6-14.8 g Density of the pellet: 9.1-9.4 g/cc

Run No.	Reaction Time (Hours) For			SS 304L corrosion rate (mpy)	Zirconium concentration in dissolvent (g/l)	Remarks
	70-80% dissolution	90-95% dissolution	95-100% dissolution			
12	24	48	72	10.4	3.6	<i>NaF was added in a single lot</i>
13		24	48	12.6	2.8	Split addition of fluoride was adopted with initial addition of 0.01M followed after 24 hr by 0.02M
14	24	72	115	7.8	2.2	Pellets were enclosed in zircaloy clad ring and <i>fluoride was added in a single lot. 80-90% dissolution was observed in 48 hours.</i>
15	24	48	72	8.3	2.8	1) Pellets were enclosed in zircaloy clad ring 2) Split addition of fluoride was adopted with initial addition of 0.01M followed after 5 h by 0.02M

Table-4 also confirms that absence of aluminium nitrate does not affect the corrosion rate of SS 304L if zircaloy is present during the dissolution process. SS corrosion rate in this series of experiments on MOX was observed to be in the range of 7.8-12.6 mpy. The results in table-4 also show that the MOX pellet dissolution was also near quantitative. Reaction completion time, however, depended on the following factors:

- Method of fluoride addition: split mode or single addition mode
- Zircaloy ring enclosing the pellets or not

Run nos. 12 & 13 show that reaction can be accelerated by split addition of fluoride. This could be on account of the lesser dissolution of zirconium ion in the dissolvent (2.8 g/l) in the split mode. In run no. 13, 0.01M fluoride concentration was maintained in the first 24 h. In this duration, more than 90% dissolution of thoria occurred.

Run nos. 14 & 15 show the effect of enclosing the pellets in zircaloy ring as in the chopped spent fuel. In run no. 14 where fluoride was added in single lot, it took nearly 115 h for completion of the reaction. When split addition mode was adopted in run no. 15, reaction time reduced to 72 hours. It appears that the initial dissolution rate of zirconium is more important than the average dissolution rate in the entire reaction period. If zirconium is made to dissolve slowly in the early stages, the overall reaction time might reduce. In the split addition mode, since fluoride content is less in the dissolvent in the early stages, zirconium dissolution rate also decreases resulting in faster dissolution of thoria/MOX.

4.2 Experiments on selective dissolution of uranium in the MOX pellet

In the MOX pellets used for experiments, 4% by weight is contributed by uranium dioxide. UO_2 forms solid solution in the MOX pellet. It is known that UO_2 is readily soluble in concentrated nitric acid. Fluoride catalysis is not required for this reaction. It was felt that it would be advantageous to selectively dissolve the uranium portion in the MOX pellet without employing fluoride catalyst initially. However, these experiments on sintered pellets were unsuccessful. This could be on account of the limited porosity of the sintered pellet. Density measurements of thoria/MOX pellets in many experiments indicated that it approached theoretical density, 10.04 g/cc implying the non-porous nature of the pellets.

Experiments were also done on MOX pellets using electrolytically generated Ce(IV) and Ag(II) ions in 13M nitric acid. These ions are powerful oxidizing species and can oxidize the uranium(IV) in UO_2 to U(VI) state. This was expected to destabilize the highly stable MOX lattice structure. However, the results in this case were also negative with the pellets, presumably on account of the low porosity of the pellets. When finely powdered MOX was used in the experiments, selective dissolution of uranium was observed to be possible to the extent of about 90%. It is

expected that the irradiated pellets in the nuclear reactor would be sufficiently porous to be amenable to selective dissolution of uranium portion without use of fluoride catalyst.

4.3 Dissolution studies at 0.01M sodium fluoride concentration

In the foregoing discussion, it was established that aluminium nitrate addition was not necessary during zircaloy-clad thoria/MOX dissolution and was avoided in all the subsequent experiments. In the following paragraphs, effect of lowering fluoride concentration from 0.03M would be reported. Fluoride is a corrosive species. After dissolution, the feed is subjected to THOREX solvent extraction process for U,Pu and Th recovery and the resultant high level radioactive waste is subjected to evaporative concentration and vitrification steps. Fluoride in the form of corrosive HF vapour can escape from HLW during evaporation and vitrification. Loss of HF during evaporation was observed to be less and it was about 2%, [7]. During vitrification, the losses were reported to be 8-9% [8]. HF in the off-gas could enhance the corrosion of off-gas equipment. Therefore, it is always desirable to reduce the concentration of fluoride that is used during dissolution reaction.

Experiments were undertaken to study the dissolution reaction kinetics for thoria and MOX pellets at concentrations below the standard 0.03M concentration.

Results of thoria dissolution at 0.01M NaF concentration were shown in table-5. In these experiments, split addition of fluoride was adopted. This was done by maintaining initial fluoride concentration at 0.005M followed by 0.01M after 3h of reaction period. In all these experiments, *the thoria pellet was enclosed in zircaloy clad ring*. At the end of 3h reaction period, 12-14% dissolution occurred in these experiments implying build up of about 0.1M thorium ion concentration in the dissolvent.

Table-5: Zircaloy-enclosed sintered Thoria pellet dissolution in 13M nitric acid in the presence of zircaloy and 0.01M NaF under boiling and reflux conditions

Run no.	Reaction Time (hours) for				SS 304L corrosion rate(mpy)	Zirconium concentration in dissolvent (g/l)	Density of pellet (g/cc)
	70-80% dissolution	80-90% dissolution	90-95% dissolution	95-100% dissolution			
16	24		48	72	8.6	0.86	8.65
17	24	48		72	8.8	1.02	8.67
18	24	48	72	96	8.4	0.73	9.96

Table-5 shows that at 0.01M fluoride concentration also, quantitative dissolution of thoria pellets occurred. SS corrosion was less than 9 mpy, about 10-15% less than the average values (10 mpy) obtained for 0.03M fluoride experiments. Interestingly, the reaction time was only 72 hours in low density pellets (run nos. 16&17). This was the reaction time observed at 0.03M fluoride concentration (table-3&4). In the experiment with denser pellet in run 18, the reaction time increased to 96 hours with 95% being complete in 72 h. It appears that by adopting split addition of NaF, zirconium dissolution rate in the reaction mixture can be lowered in the early stages of reaction and faster thoria/MOX dissolution rates can be achieved *without the need for higher fluoride concentration*. Zirconium ion concentration at the end of the reaction, as the table-5 shows, is about 0.01M matching with the fluoride concentration employed and agrees with the literature which states that the zirconium concentration in this kind of systems increases to a limiting value equal to the fluoride concentration [9].

In table-6, results of experiments on MOX pellets at 0.01M NaF concentration were reported. **In all the experiments, two MOX pellets were enclosed in a zircaloy ring.** In run no. 19, NaF solution was added in single lot. In the other two experiments in table-6, split addition mode was used as in table-5.

Table-6: Zircaloy-enclosed sintered MOX pellet dissolution in 13M nitric acid in the presence of zircaloy and 0.01M NaF under boiling and reflux conditions

Run no.	Reaction Time (hours) for			SS 304L corrosion rate(mpy)	Zirconium concentration in dissolvent (g/l)	Density of pellet (g/cc)	
	50-60%	70-80% dissolution	80-90% dissolution				95-100% dissolution
19	24	48	72	119	8	1.2	9.51
20		24	48	72	9	0.7	8.84
21	24	48	72	96	11	1.2	10.02

The results in table-6 show that the reaction time was dependent on multiple factors including pellet density, zirconium ion concentration and mode of fluoride addition. Comparing run nos. 20&21, pellet in run 21 is denser by about 12%. Its density is 95% of theoretical density (10.04 g/cc). Besides, dissolved zirconium ion concentration in run no. 21 is higher by a factor of nearly two. All these factors could be responsible for the observed longer reaction time in run no. 21 in comparison with run no.20. In run no. 19, the density of pellet is only 5% lower than that used in run no.21. In the run no. 19, fluoride was added in a single lot. Zirconium concentration is also higher compared to that in run no. 20. All these factors might have contributed to the much longer reaction period of 119 hours. *It can be concluded that the reaction time in the dissolution of thoria/MOX dissolution is 72-96h depending on pellet density when split addition mode of fluoride addition is adopted.*

4.4 Dissolution studies on thoria at 0.005M fluoride concentration

Table-7 gives the data at **0.005M** sodium fluoride concentration for thoria pellets. Corrosion of SS 304L has reduced further at this lower fluoride concentration. It varied from 3.5 to 8.6 mpy (ca. table-5). It took 72-94 hours to complete 90-95% dissolution in most runs.

Table-7: Thoria pellet dissolution at 0.005M NaF concentration; Mode of NaF addition: split mode with 24 h interval in two equal proportions under boiling and reflux conditions

Run no.	Reaction Time (hours) for					SS 304L corrosion rate (mpy)	Zirconium concentration in dissolvent (g/l)
	60-70%	70-80%	80-90%	90-95%	95-100%		
22	48	72	100		122	3.5	0.1
23		48		72	96	6.4	0.31
24	48		72	95	115	---	0.4
25	48		70	94	123	4.8	0.26
26*	24	48		72	120	8.6	0.41

* 3 hours interval in the split mode of fluoride addition instead of 24 hours; zircaloy ring enclosed the pellet; pellet density: 9.9 g/cc

Further progress was monotonous and required about 120 hours. Zirconium concentration in these experiments was observed to be mostly in the range of 0.3-0.4 g/l (0.003-0.004M). Once again, the zirconium concentration during dissolution reaction reached a limiting concentration equal to that of fluoride in the reaction mixture. These results clearly show that NaF concentration as low as 0.005M (1/6th of the presently used value) could also be employed in split mode to achieve >90% dissolution of thoria in 72-96h. Reaction time for further dissolution would be more than 100 hours. Reactor-irradiated pellets are prone to damage and cracks and, therefore, are expected to dissolve faster even at lower fluoride concentrations.

In table-8, results of MOX dissolution at 0.005M NaF concentration were presented. Reaction time for completion was up to 120 hours with >90% dissolution in 90-96 hours. Zirconium average concentration in the dissolvent was 0.46 g/l (0.005M) matching the concentration of fluoride used in the reaction. Average corrosion rate of SS 304L was < 8 mpy in the MOX dissolution.

Table 8-: MOX dissolution at 0.005M NaF concentration under boiling and reflux conditions

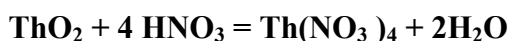
Run no.	Reaction Time (hours) for					SS 304L corrosion rate (mpy)	Zirconium concentration in dissolvent (g/l)	Remarks
	50-60%	70-80%	80-90%	90-95%	95-100%			
27		28	48		72	7.6	0.76	Fluoride was added in single lot; single MOX pellet was used in the experiment
28		24		48	72	7.5	0.25	Split mode of fluoride addition with 24 h time gap; two MOX pellets were used in this experiment
29	24			90	120	8.5	0.38	--do--
30	24	48	72	96	120	7.0	0.46	Split mode with 3h time gap; pellet density:9.52 g/cc; zircaloy enclosed the two pellets

4.5 Feasibility experimental studies to enhance reaction rate of thorium dissolution at $\leq 0.005M$ fluoride concentration

As mentioned previously in the report, dissolution rate of thorium depends on nitric acid concentration as shown below:

$$-\frac{d}{dt} [\text{ThO}_2] = k [\text{HNO}_3] [\text{HF}]^{0.5}$$

As thorium dissolves in the reaction mixture, HNO_3 concentration decreases as per the following reaction:



As nitric acid concentration decreases, the rate of dissolution also decreases. Most of the aforementioned experiments were conducted at 13M nitric acid volume to thorium/MOX ratio of ~4.0. This was done, as mentioned earlier, so that the resultant dissolvent can be fed to THOREX solvent extraction process without requirement of acid killing step. It was felt that, if initial nitric acid (13M) to thorium pellet weight is increased from 4.0 to a higher value, the reaction rate should increase. Experiments were conducted under boiling and reflux conditions at higher ratio of 10:1 to verify

this assumption. In table-9, the results were presented. In these feasibility experiments, SS and zircaloy coupons were not introduced into the reaction mixture.

Table-9: Thoria pellet dissolution at 13M nitric acid volume to thoria weight ratio=10
*ratio of acid to pellet weight is~4.0

Run no.	Reaction Time (hours) for					NaF concentration (M)
	50-60%	70-80%	80-90%	90-95%	95-100%	
31	24	46		67	90	0.003
32	22	48	67		90	0.003
33*	24	48			120	0.003
34		24	48		67	0.004
35		22	46		67	0.005
36*	24	46	67	91	119	0.005

It is clear from the table-9 that when the ratio was maintained at 10, the reaction time was only 67 hours at 0.005M (run nos. 34, 35). When the ratio was lowered to 4, the reaction time increased to 119 hours (run no. 36). In the experiments at 0.003M NaF concentration at ratio of 10, the reaction time was 90 hours. When the ratio of acid volume to pellet was reduced to about 4.0, the reaction time increased to 120 hours. These results show that higher volume of 13M nitric acid relative to pellet weight leads to significant lowering of reaction times even at fluoride concentrations as low as 0.005M. This increase in acid volume necessitates acid killing step for the downstream THOREX solvent extraction process.

An alternative approach could be extractive dissolution reaction. This involves periodic removal of thorium ions (at least partially) from the dissolver solution by Purex solvent extraction. This would enhance the free fluoride ion content in the dissolvent and hence the reaction rate. Preliminary experiments in this direction have shown that the reaction time at 0.005M fluoride concentration could be reduced to 54 hours (ca. 96 hours in the normal mode of reaction).

Another possibility could be to use partial reflux instead of total reflux to have higher concentration of acid during the reaction. In this mode of operation, since there will be some loss of water from the dissolvent by evaporation, the concentration of acid will be higher than in the total reflux system. This might enhance the rate of thoria dissolution.

Feasibility studies on rate enhancement using ultrasound were conducted using ultrasonic horn. It was observed that the effect is more pronounced when thorium pellet is broken into pieces. Effect on the sintered pellet was not significant. Further experiments are in progress to explore the potential of the different approaches attempted in this section.

5. Thorium Dissolution Experiments at 500g scale

Thorium dissolution experiments described in the earlier sections were conducted using a single pellet at a time. The experiments were, subsequently, conducted at 500 g scale to confirm the laboratory scale findings. In these experiments, 30 sintered Thorium pellets were encased in zircaloy-2 tubes, two in each of 15 zircaloy tubes (40 mm long). These pellets were placed in a 5 litre round bottom borosilicate glass flask containing two litres of 13M nitric acid and sodium fluoride catalyst. Six coupons of SS 304L having total surface area of 90 cm² were placed in the reaction solution. *Aluminium nitrate addition was avoided in these experiments also.* The contents of the flask were heated to gentle boiling under reflux using mantle heater. The experiments were done at 0.01 and 0.005M sodium fluoride catalyst concentration. Catalyst solution was added in split mode as explained previously. Results were shown in table-10.

Table-10: Zircaloy-clad Thorium dissolution at 500 g scale

Run no.	NaF concentration (M)	Reaction Time (hours) for						SS 304L corrosion rate (mpy)	Zirconium concentration in dissolvent M
		40-50%	60-70%	70-80%	80-90%	90-95%	95-100%		
37	0.01		24	48	72		96	9.5	0.0133
38	0.005	24	48	72	96	120		8.2	0.0137

Results presented in table-10 confirm the trends obtained in smaller scale experiments.

5. Conclusions

In the present study, Thoria and Thoria-Urania MOX (96 weight% ThO₂ & 4 weight % UO₂) dissolution at three different sodium fluoride concentrations, viz., 0.03, 0.01 and 0.005M were studied. In addition, effect of avoiding aluminium nitrate addition during dissolution reaction was studied on corrosion of SS 304L in the presence of zircaloy clad material. These experimental results clearly showed that when zircaloy clad material is present during dissolution of thoria and MOX, addition of aluminium nitrate is not necessary for mitigating corrosion. This would have beneficial impact on downstream HLW vitrification process. It would lead to enhanced waste loading. It will also reduce foaming and viscosity related problems during vitrification step.

SS 304L corrosion rate studies at 0.03M NaF concentration clearly showed that if zircaloy is present, the corrosion rate of this alloy in presence and absence of aluminium nitrate is quite comparable and it is about 10 mpy. The corrosion rates reduced with the reduction in fluoride concentration used.

Fluoride concentration can be reduced from the presently adopted 0.03M to lower concentrations by following the procedure of adding fluoride into the dissolver in two equal proportions with time gap of about 3-4 hours. Reaction times for dissolution reaction were observed to be 48-72, 72-96 and 96-120 hours for 0.03, 0.01 and 0.005M respectively depending on density of the sintered pellets used. Average corrosion rate of SS 304L was 10, 8.5 and 6.5 mpy for fluoride concentrations of 0.03, 0.01 and 0.005M respectively during the dissolution reaction.

Preliminary studies showed that enhancing volume of 13M nitric acid during the dissolution reaction can reduce the reaction time from 96 to about 67 hours at 0.005M concentration.

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References

1. M.E.Shying, T.M.Florence and Carswell, 'Oxide Dissolution Mechanisms-1, The Role of fluoride in the Thoria/Nitric/Hydrofluoric acid System', J.Inorg.Nucl.Chem. 32(1970):3493-3508
2. M.E.Shying, T.M.Florence and D.J. Carswell, 'Oxide Dissolution Mechanisms-II, A mechanism for the thoria/nitric/hydrofluoric acid system', J.Inorg.Nucl.Chem. 34(1972):213-220
3. R.S.Ondrejcin and B.D.Mclaughlin, 'Corrosion of high Ni-Cr alloys and type 304L Stainless steel in HNO₃-HF', Report No. DP-1550(1980), Savannah River Laboratory, Aiken, SC, USA
4. L.G.Sillen, Compiler. 'Stability Constants of Metal-ion complexes'. Special Publication no. 17, The Chemical Society, London (1964).
5. B.L.Vondra,'Alternate Fuel Cycle Technologies/Thorium Fuel Cycle Technology Programs Quarterly Report for Period October 1 to December 31, 1977, ORNL/TM-6206, pp. 3-5, ORNL (Feb. 1978)
6. M.S.Farrell, S.R.Isaacs and M.E.Shying, 'Laboratory Development of the Grind-Leach process For the H.T.G.C.R. Fuel cycle, Pat 2. Dissolution of Beryllia in nitric acid solutions', Report No. AAEC/E154 (June, 1966)
7. C.P. Kaushik et.al., "Fluoride Mapping during Concentration of Simulated High Level Radioactive Liquid Waste", NUCAR-2009, Mithibai College, Mumbai, January 7-10, 2009.
8. C.P.Kaushik et.al., Unpublished report, BARC
9. O.K.Tallent et.al., 'The effects of zirconium on the dissolution rate of thoria in nitric-hydrofluoric acid solutions', Nuclear Technology, 60(March,1983): 395-405.