

## **OPTIMIZATION OF DISSOLUTION PROCESS PARAMETERS FOR URANIUM ORE CONCENTRATE POWDERS**

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### **ABSTRACT:**

Nuclear fuel complex processes Uranium Ore Concentrate (UOC) for producing uranium dioxide powder required for the fabrication of fuel assemblies for Pressurized Heavy Water Reactor (PHWR)s in India. UOC is dissolved in nitric acid and further purified by solvent extraction process for producing nuclear grade  $\text{UO}_2$  powder. Dissolution of UOC in nitric acid involves complex nitric oxide based reactions, since it is in the form of Uranium octa oxide ( $\text{U}_3\text{O}_8$ ) or Uranium Dioxide ( $\text{UO}_2$ ). The process kinetics of UOC dissolution is largely influenced by parameters like concentration and flow rate of nitric acid, temperature and air flow rate and found to have effect on recovery of nitric oxide as nitric acid. The plant scale dissolution of 2 MT batch in a single reactor is studied and observed excellent recovery of oxides of nitrogen ( $\text{NO}_x$ ) as nitric acid. The dissolution process is automated by PLC based Supervisory Control and Data Acquisition (SCADA) system for accurate control of process parameters and successfully dissolved around 200 Metric Tons of UOC.

The paper covers complex chemistry involved in UOC dissolution process and also SCADA system. The solid and liquid reactions were studied along with multiple stoichiometry of nitrous oxide generated.

**Key words:** *UOC, Dissolution, reaction kinetics, oxides of nitrogen, Nitric acid, SCADA.*

### **INTRODUCTION**

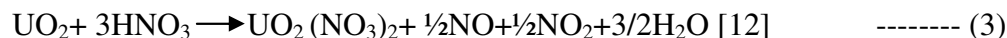
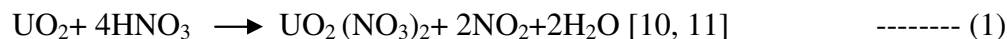
Nuclear Fuel Complex an industrial unit of department of atomic energy manufactures PHWR and BWR fuel assemblies to various atomic power reactors in India. Uranium Oxide Plant at NFC produces ceramic grade uranium dioxide powder using imported Uranium Ore Concentrate (UOC) and process rejects such as sintered  $\text{UO}_2$  pellets, powder and grinding sludge etc. The process employs various unit operations like dissolution, solvent extraction, precipitation, filtration, drying, calcination, reduction and stabilization. The process rejects are generated due to stringent specifications of chemical and nuclear purity and also physical and metallurgical characteristics assigned to the fuel. Dissolution of UOC in nitric acid involves complex nitric oxide based reactions, since it is in the form of Uranium Dioxide ( $\text{UO}_2$ ) or Uranium octa oxide ( $\text{U}_3\text{O}_8$ ). The dissolution of Uranium Ore Concentrate was a major challenge in the production flow sheet of uranium oxide plant due to its varied chemical nature and hazards associated with it. Efforts have been made to develop an economic and eco-friendly process for dissolution of UOC by satisfying the basic principles of green chemistry. The kinetics of dissolution of these materials

is extensively studied at plant scale [1-6] for processing of bulk quantity of Uranium Ore Concentrates.

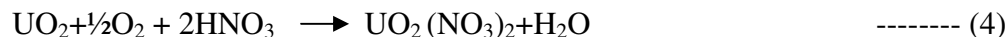
The application of this model to predict UO<sub>2</sub> dissolution rates in aqueous solutions containing either dissolved oxygen or hydrogen peroxide is described [9-10]. The chemical dissolution described in above studies usually carried out in boiling nitric acids of 2 M to 12 M concentrations. The present dissolution method is controlled and oxidative in nature. This study reveals the effect of various parameters like temperature, flow rate of acid, air flow rate, concentration of uranium in raw material, various reaction mechanisms, and Spontaneous Dissolution Rates (SDR). The authors have also established the process parameters like temperature, flow rate of nitric acid and flow rate of air.

#### CHEMICAL DISSOLUTION

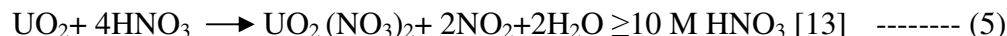
The following reactions are involved in the various forms of uranium dissolution.



In presence of oxygen, the following reaction takes place



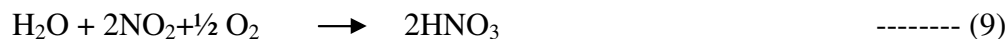
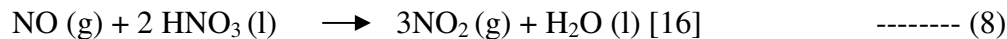
According to Benedict et al, the main component of NO<sub>x</sub> changes from NO to NO<sub>2</sub> at 10 M of nitric acid



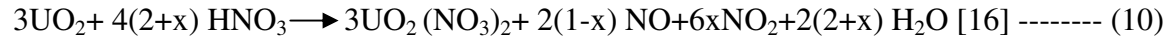
E. Henrich et al. have shown the following reaction between 2 M-7 M of nitric acid



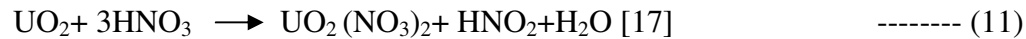
Hermann et al, measured concentration of NO<sub>2</sub>/NO ratio at 363 K ~1 for 4.85 M and 1.3 for 6.1 M HNO<sub>3</sub>. As per Tsutomu sakurai et al, UO<sub>2</sub> dissolves in a HNO<sub>3</sub> solution according to the equation (5)&(6) and the part of NO thus produced is rapidly converted to NO<sub>2</sub>. The amount of NO<sub>2</sub> generated is lesser than the above when oxygen is sparged through dissolution solution where NO gets converted to NO<sub>2</sub>



The equilibrium constant of the above reaction equation (8) controls the NO<sub>x</sub> composition in the dissolution. Therefore, the dissolution is apparently expressed as follows, by taking x as fraction of NO converted to NO<sub>2</sub> (0<x<1)



Tetsuo Fukusawa et al, also emphasized the influence of nitrous acid decomposition on dissolution reaction



This is followed by decomposition of nitrous acid

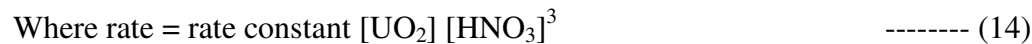


Continued together it forms

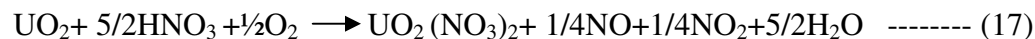
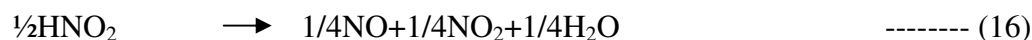


From above equations authors have evolved four mechanisms of dissolutions.

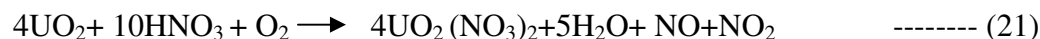
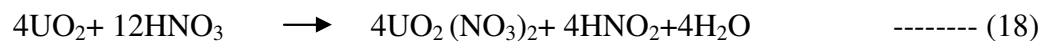
**Mechanism-I** contains the equation (11 & 12) that forms the components of equation (3)



**Mechanism-II** has Sparging of oxygen through dissolution solutions contains equation (11&12) followed by equation (16) which gives the same rate as equation (13)

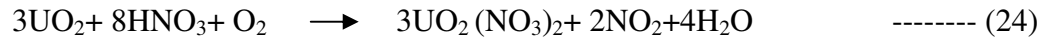
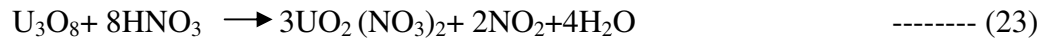


**Mechanism –III** has the same rate as equation (14)



**Mechanism – IV**





The overall rate equation for dissolution reaction is

$$\text{Rate of dissolution} = k_1 k_2 A [\text{O}_2] [\text{NO}_3^-] / k_1 [\text{O}_2] + k_2 [\text{NO}_3^-] \quad \text{----- (25)}$$

Where  $k_1$  and  $k_2$  are constants,  $[\text{O}_2]$  is the concentration of depolarizing agent oxygen in air,  $[\text{NO}_3^-]$  is the concentration of  $\text{NO}_3^-$  complexing agent and  $A$  is the total surface area of powder in contact with solution. At higher Molarity,  $\text{O}_2$  concentration in solution becomes negligible, hence the equation (25) reduces to

$$\text{Rate} = k_1 A [\text{O}_2] \quad \text{----- (26)}$$

This implies that the rate of dissolution under these conditions depends on the concentration of  $\text{O}_2$  in water. It means in high acidity, the requirement of  $\text{O}_2$  is very high. This can be achieved by increasing the flow of oxygen in solution. This is demonstrated successfully by G.I.Miles [22] by high temperature and high acidity dissolution.

The authors have looked into the second possibility where dissolution is carried at low acidity i.e  $\text{NO}_3^-$  concentration is low and then the rate equation (25) becomes

$$\text{Rate} = k_2 A [\text{NO}_3^-] \quad \text{----- (27)}$$

This implies that the rate of dissolution is function of the concentration of acid.

### **3. PLANT SCALE DISSOLUTION TRIALS**

To understand the above requirements in detail, plant scale trials were carried out in semi-batch and slightly pressurized dissolution reactor. UOC powders contain particles of various sizes and specific surface areas. This powder is charged into the reactor as batch by pneumatic transfer system and nitric acid is added subsequently at a required rate.

The initial loading of UOC powders is around 1.5MT to 2MT. In order to obtain 2.0 to 2.5 mole.l<sup>-1</sup> of uranium, nitric acid is added slowly as per the equation (27) besides maintaining aerated water with oxygen around  $0.27 \times 10^{-3} \text{ T mol.l}^{-1}$ . Initial activation energy requirement is around 64 kJ.mol<sup>-1</sup> for any form of UOC. This energy is supplied to the mass by initial heating. Once the reaction is triggered the temperature of reaction is sustained due to its exothermic nature.

The Contents in the reactor are agitated by compressed air at a flow rate of 5m<sup>3</sup>/hr. NOx generated during dissolution is passed through reflux condenser to recycle the vapors of nitrous acid and nitric acid into the reactor. The uncondensed NOx gas is passed through a series of

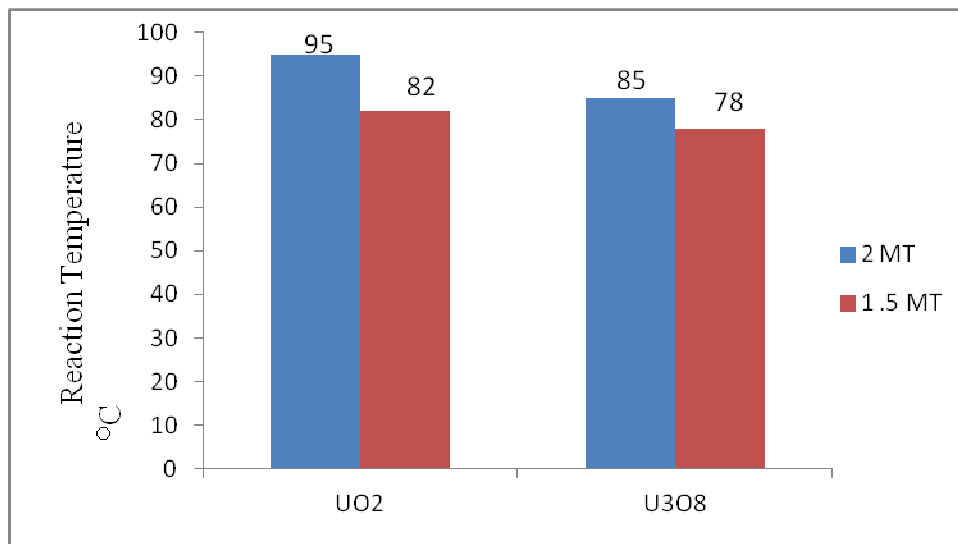
water bubblers to recover nitric acid. The remaining off gases passed through a series of scrubbers (packed column) to convert NO<sub>x</sub> to sodium nitrites/nitrates in alkali solution.

Temperature, pressure, nitric acid flow rate and level of reactor were measured using various instruments such as RTD, differential type pressure transmitters, magnetic flow meters, guided radar type level transmitters etc. This ensured precise and accurate control of process parameters for experimentation and real time monitoring at plant scale.

#### **4. Observations:**

##### **4.1. Maximum operable dissolution reaction temperature for U<sub>3</sub>O<sub>8</sub> and UO<sub>2</sub>**

Various experiments were performed to assess the maximum temperature for batch sizes 1.5MT and 2MT UOC powder. Figure-1 shows the comparison of U<sub>3</sub>O<sub>8</sub> and UO<sub>2</sub> type of raw material and their maximum operable reaction temperature during dissolution with no change in other parameters. This temperature was finalised for safe handling of NO<sub>x</sub> generated during dissolution for the existing plant set up.

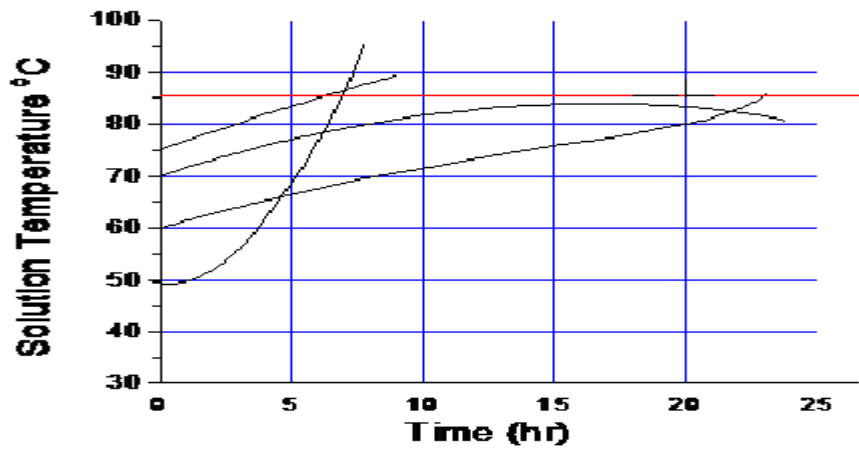


**Figure 1: Maximum operable reaction temperature during dissolution**

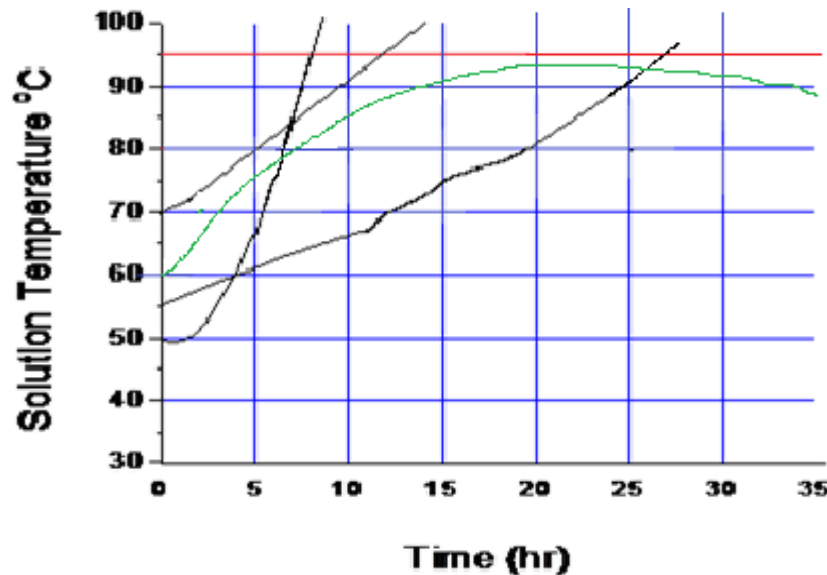
##### **4.2. Initial temperature for dissolution**

Trials were initiated with various temperatures to fix initial temperature for dissolution. Figure-2 indicates the effect of initial temperature on dissolution reaction for U<sub>3</sub>O<sub>8</sub> type of raw material, if the temperature is selected below 70°C or above 70°C the maximum operable temperature approaches faster and reaction becomes uncontrolled. Hence 70°C is set as initial starting temperature for U<sub>3</sub>O<sub>8</sub> type of raw material. Similar trials were repeated for UO<sub>2</sub> dissolution it was observed that 60°C as initial temperature was the optimum choice for dissolution of UO<sub>2</sub> as it

evident in Figure-3. For mixture of both  $U_3O_8$  and  $UO_2$  raw materials the starting temperature chosen was 65 °C which was an appropriate choice.



**Figure 2:** Progress of reaction for various initial temperatures in the case of  $U_3O_8$  type UOC dissolution



**Figure 3:** Progress of reaction for various initial temperatures in the case of  $UO_2$  type UOC dissolution

#### 4.3. Nitric acid flow rate

Above trials were done at low flow rate (60 lit/hr) and then efforts were initiated to increase the nitric acid flow rate to optimize dissolution process. Nitric acid flow rate was increased from 60 to 80lit/hr for both type of raw materials. Figure-4 indicates that when the flow rate were increased from 60 lit/hr to 80lit/hr after 5hrs, the maximum dissolution temperature did not cross maximum permissible operating temperature. Hence the nitric acid flow rate was kept 60lit/hr for

5 hrs and then increased to 80 lit/hr for the entire dissolution cycle. Similarly Figure-5 indicates effect of increase in nitric acid from 60 lit/hr to 80lit/hr and it was observed that in case of  $\text{UO}_2$  type of raw material the maximum operating temperature is not reaching within five hours and reaction becomes sustained; hence the same parameter was selected for  $\text{UO}_2$  type of UOC raw material.

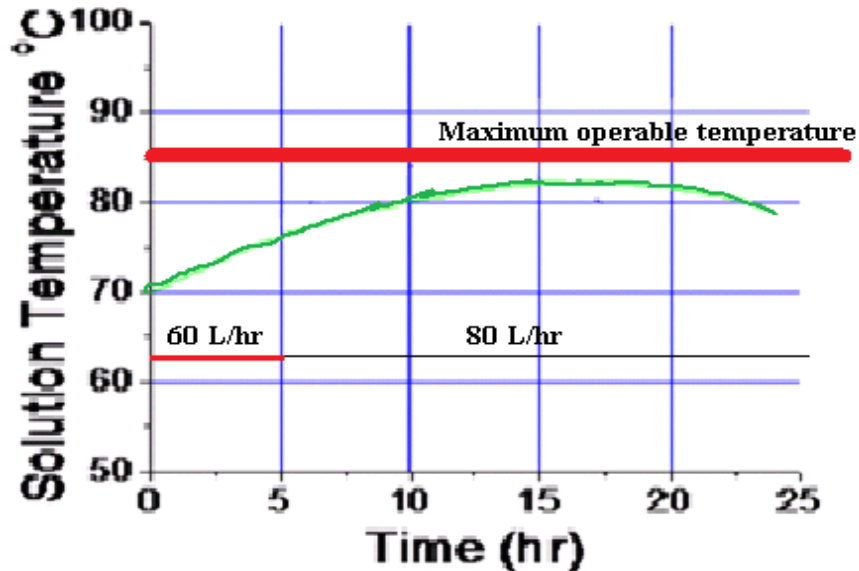


Figure 4: Progress of dissolution reaction for different nitric acid flow rate in the case of  $\text{U}_3\text{O}_8$  dissolution

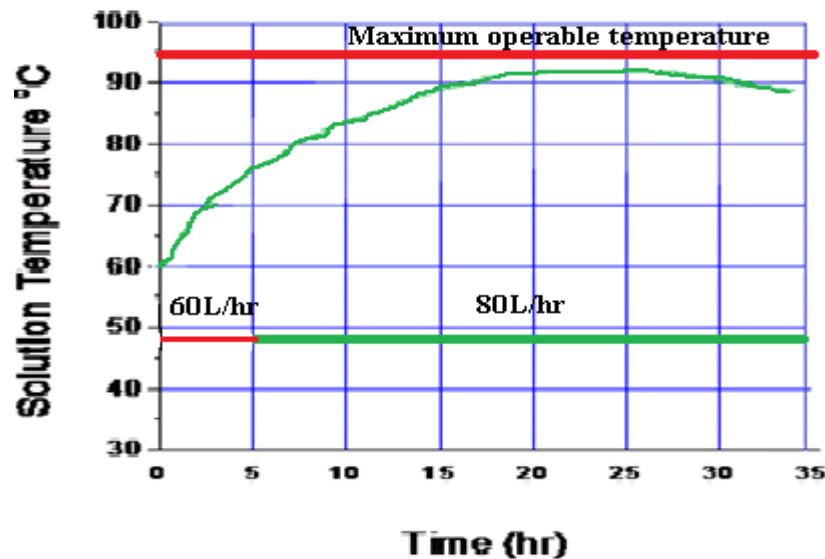
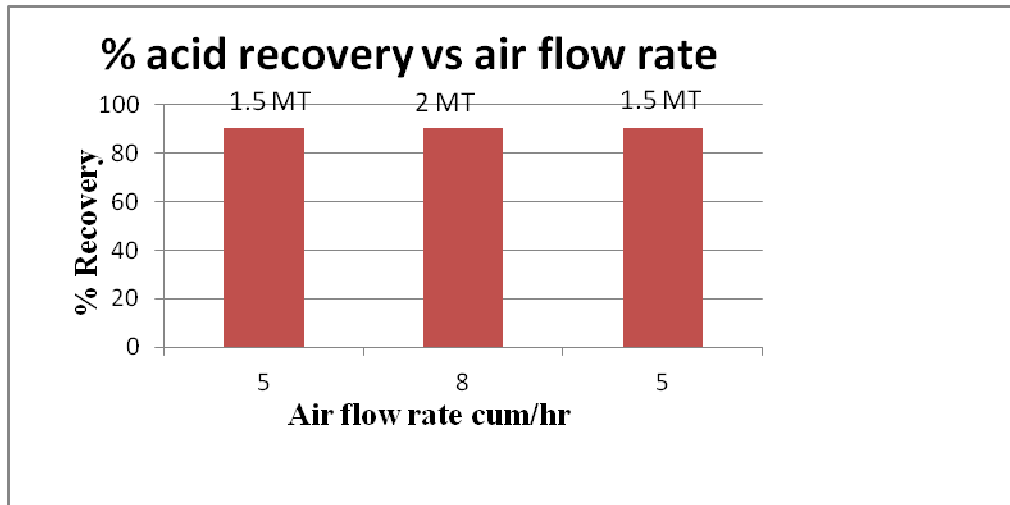


Figure 5: Progress of dissolution reaction for different nitric acid flow rate in the case of  $\text{UO}_2$  dissolution

#### 4.4. AIR FLOW RATE

The effect of air flow rate at 5m<sup>3</sup>/hr for a 1.5MT batch helped in recovery of nitrous oxide as nitric acid with 90% efficiency. The different air flow rates such as 5m<sup>3</sup>/hr and 8m<sup>3</sup>/hr was studied for a 2MT batch. It has been observed that there was no significant change in recovery of nitric acid at increased flow rate also. This could be due to various substoichiometric reactions of nitric acid with different oxidation states of Uranium.



**Figure 6:** Percentage NOx recovery of dissolution reaction for different air flow rates for different batch sizes

#### 5. SPONTANEOUS DISSOLUTION RATES

SDRs of the pellets are determined to elucidate the dissolution chemistry and to obtain empirical mathematical equations for calculating process variables such as nitric acid concentration, oxidizing agents etc.

Dissolution rate equation given by  $dW/dt = W_0 d\phi/dt = a \cdot IDR$  ----- (28)

Where W denotes the dissolved weight of UO<sub>2</sub> pellet, W<sub>0</sub> the initial weight of uranium,  $\phi$  the fraction of dissolved UO<sub>2</sub> pellet, t the time, a effective dissolution area and IDR the dissolution rate per unit area.

The effective dissolution area can be given by;

$$a = a_0 F(\phi) \text{ ----- (29)}$$

Where a<sub>0</sub> is the initial effective dissolution area and F( $\phi$ ) the ratio of effective dissolution area at a fraction of  $\phi$  to the initial effective dissolution area. When there are no cracks,



dissolution occurs axially then the dissolution of spherical or cubic  $\text{UO}_2$  pellet has the change in  $F(\phi)$  given by eq.(30) assuming dissolution occurs uniformly at the surface

$$F(\phi) = (1 - \phi)^{2/3} \quad \text{----- (30)}$$

Fukasawa et al., have given the following rate of dissolution

$$d\phi/dt = a_0 / W_0 (1 - \phi)^{2/3} [6.3 \times 10^5 \exp(-7,654/T)] C_H^2 \quad \text{----- (31)}$$

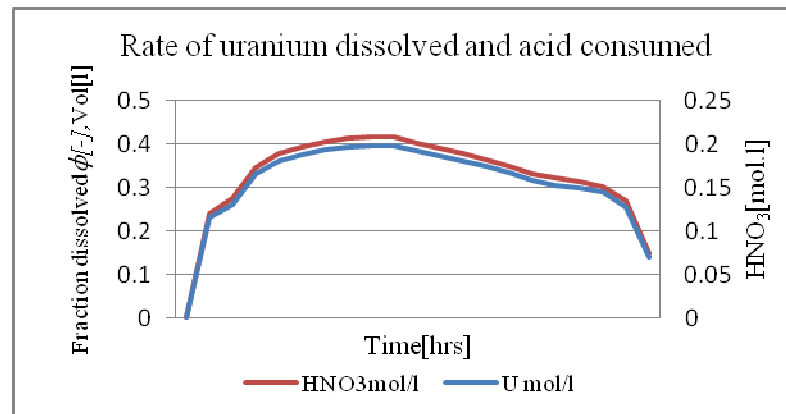
Where  $C_H$  concentration of acid

$$k = A e^{B/T} \quad \text{----- (32)}$$

$k$  is dissolution rate constant ( $6.3 \times 10^5 \exp(-7,654/T)$ ),  $A$  denotes the constant and  $B$  the apparent activation energy.

## 5.1. RESULTS AND DISCUSSION

Fig.7 shows the change in the fraction of dissolved  $\text{UO}_2$  pellet. In the figure the measurement of dissolution time was started after heating was done. The fraction of dissolved  $\text{UO}_2$  pellet was determined by calculating  $C_U(t)V(t)/W_0$ , where  $C_U$  denotes the measured uranium concentration at time  $t$  and  $V$  the measured volume of dissolver solution at time  $t$ .



**Figure.7:** Change in fraction dissolved with time

**Table: 1** SDR'S of present and previous studies

Authors	Fuel	SDR(kg.min <sup>-1</sup> .m <sup>-2</sup> )	$K$
Present study	PHWR	$k(C_{H0})^{0.2}$	$7.2 \times 10^6 \exp(-4,735/T)$
Fukasawa <i>etal.</i>	LWR	$k(C_{H0})^{2.8}$	$6.3 \times 10^5 \exp(-7,654/T)$

Authors	Fuel	SDR(kg.min <sup>-1</sup> .m <sup>-2</sup> )	K
Nemoto <i>etal.</i>	LWR	$k(C_H)^{1.74}$	$9.62 \times 10^4 \exp(-5,535/T)$
Ohsaki <i>etal.</i>	LWR	$k(C_H)^2$	$7.54 \times 10^7 \exp(-7,549/T)$

Present study shown in Table 1; the SDR based on equations (31&32), then the rate is

$$d\phi/dt = a_0 / W_0 (1 - \phi)^{2/3} [7.2 \times 10^6 \exp(-4,735/T)] C_H^2 \quad \text{----- (33)}$$

The dissolution rate constant of present study is comparable with the earlier works although the dissolution is carried at lower acidity.

Hideaki Mineo *etal*[23].for the powders of diameter D density of  $\rho$  the value of  $a_0/W_0$  can be estimated by

$$a_0/W_0 = 6/\rho D \quad \text{----- (34)}$$

Table.2 summarizes the findings of present study H.Mineo *etal*, Tsukada and Ikeda *etal*, and dissolution conditions and it also lists up the values of  $a_0 / W_0$  and other values used in the calculation. In case of spent fuel, Ikeda *etal*, findings were noted considering stoichiometric mole ratio of uranium to nitric acid was 3/8 equation (2), where as the present study considers ratio of one to two.

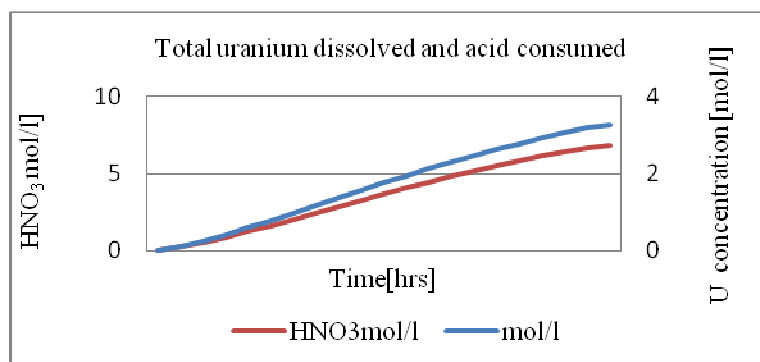
**Table 2:** Dissolution conditions and parameters

Authors	Fuel (burn up [MWd.t <sup>-1</sup> ])	Pellet (L <sub>0</sub> [m]) or Powder(D[m])	Weight [X10 <sup>-3</sup> kg]	Acidity [mol.l <sup>-1</sup> ] (V[dm <sup>3</sup> ])	Dissolution Temperature [K]	$a_0/W_0$ [m <sup>2</sup> .kg <sup>-1</sup> ]
Present study	PHWR	Pellets 0.016	2300000	0.2	343	1.75
Present study	PHWR	Pellets 0.016	2300000	0.2	353	1.9
Present study	PHWR	Pellets 0.008	2300000	0.2	343	1.79
Present study	PHWR	Pellets 0.008	2300000	0.2	353	1.95
H.Mineo <i>etal.</i>	PWR 44300	Pellets 0.04	328.86	5 (1.51)	353	0.03107
H.Mineo <i>etal.</i>	PWR 44300	Pellets 0.04	356.64	5 (1.49)	363	0.05734

H.Mineo <i>etal.</i>	PWR 44300	Pellets 0.04	399.88	5.14(1.49)	373	0.0048
Tsukada <i>etal.</i>	LWR 68000	Pellets 0.03	17.59	4 (0.09)	375	0.037
Tsukada <i>etal.</i>	LWR 68000	Pellets 0.03	17.99	7(0.09)	375	0.037
Present study	PHWR	Powder 0.1-30X10 <sup>-6</sup>	2300000	0.1	296	8
Present study	PHWR	Powder 0.1-30X10 <sup>-6</sup>	2000000	0.1	296	8
Ikeda <i>etal.</i>	PWR 50000	Powder 90-150X10 <sup>-6</sup>	1.032	3.1 (0.3)	298	4.9
Ikeda <i>etal.</i>	PWR 50000	Powder 300-355X10 <sup>-6</sup>	1.051	3.1 (0.3)	298	1.79
Ikeda <i>etal.</i>	PWR 50000	Powder 850-1000X10 <sup>-6</sup>	1.076	3.1 (0.3)	298	0.636
Ikeda <i>etal.</i>	PWR 50000	Powder 300-355X10 <sup>-6</sup>	1.059	2.5 (0.3)	296	1.79
Ikeda <i>etal.</i>	PWR 50000	Powder 300-355X10 <sup>-6</sup>	1.096	3.5 (0.3)	298.5	1.79
Ikeda <i>etal.</i>	PWR 50000	Powder 300-355X10 <sup>-6</sup>	1.033	4 (0.3)	298.5	1.79

The powder dissolution rates are spontaneous and for pellets SDRS are low but still show higher values when compared to Ikeda *etal.* The direct relationships between higher dissolution rates and higher surface area have been confirmed. The dissolution rates at 353K have been plotted in Fig.7 and Fig.8. The initial sluggishness in reaction rate is due to very low surface area which is almost doubled at the end of the first hour dissolution. This is due to roughening of surface impinging nitric acid and oxidation in oxygenated conditions. The dissolution rate at the end of reaction is bit low and maintained at the second power of the nitric acid plus one-half the nitrate from uranyl nitrate instead of increasing as the second power of the total nitrate concentration as indicated in the Fig.7&8

$$\text{The decreased rate} = c[M.HNO_3 + M.UO_2(NO_3)_2]^2 \quad \text{----- (35)}$$



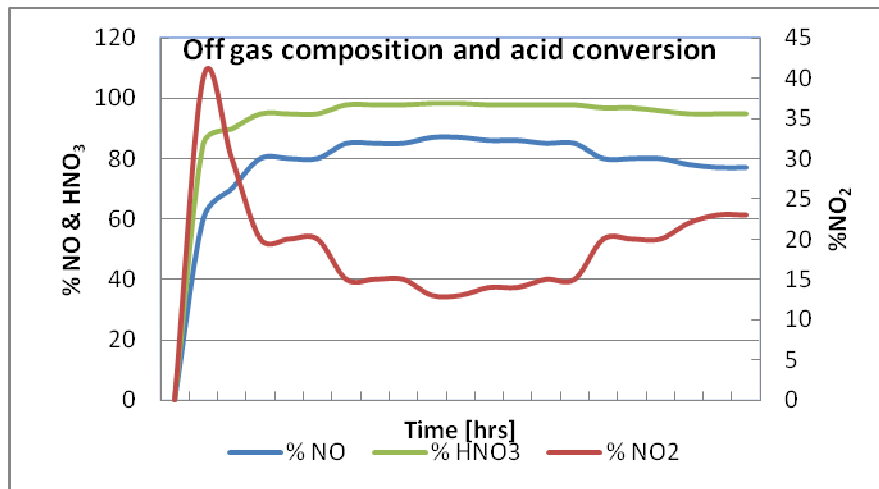
**Figure 8:** Uranium dissolved and acid consumed with progress in time

Table 3:

Authors	Acidity [mol.l <sup>-1</sup> ]	No.Of Moles of acid required for 1 mole of U	NO	NO <sub>2</sub>
Sakurai.T <i>etal.</i>	12.5	4.9	18	82
Sakurai.T <i>etal.</i>	8.1	3.6	45	55
Sakurai.T <i>etal.</i>	6.7	2.7	75	25
Sakurai.T <i>etal.</i>	4.5	2.5	84	16
Sakurai.T <i>etal.</i>	3.4	2.6	86	14
Present study	1.5	2	97	3
Present study	1	1.8	97.5	2.5

Table 3 shows that earlier studies of Tsakurai *etal.*[24] have consumed around 4.9 to 2.66 moles of acid per mole of uranium where as the present study has shown the consumption of only 1.8 to 2 moles of acid per mole of uranium due to complete recovery of acid through aeration i.e. oxidative dissolution.

Figure 9: shows the off gas composition as expected from Table 3, predominantly NO and complete conversion into nitric acid.



**Figure 9:** Off-gas composition and conversion to nitric acid with time

For complete and rapid reaction rate, and to keep off-gases to minimum for achieving complete conversion to nitric acid, the fume less dissolution is adopted by air-tight dissolver and compressed air as an oxidizing agent for nitric acid recombination. The following reactions observed



It was always the  $\text{HNO}_2$  that formed as an intermediate product [24] as per the equations (11, 12, 16) and its decomposition into  $\text{NO}_x$  increases the rate of reaction. The reactions equations (36, 37) represented the oxidation and absorption process, and equation (38) represented the reaction dissolving a mole of uranium. Depending on the type of dissolving material whether it is a pellet or powder, the requirement of oxygen varied considerably from 0.375 to 1.375 moles. The reflux condenser placed just on the top of the dissolver drops the condensed  $\text{HNO}_3$  into the dissolver along with a set of three bubblers in series worked as perfect setup to completely convert  $\text{NO}_x$  to nitric acid as shown in Fig.9. The oxidation process was observed to be instantaneous at moderate temperature; and the absorption in water was practically instantaneous, however as the nitric acid concentration increases the absorption becomes slow. The process produced heat was used for sustaining the reaction. Therefore a moderate temperature of 343K figure.10 and low acidic reaction was initiated without any heating during the dissolution except for initiating the reaction in case of pellets, at start of dissolution as given in figure.10.

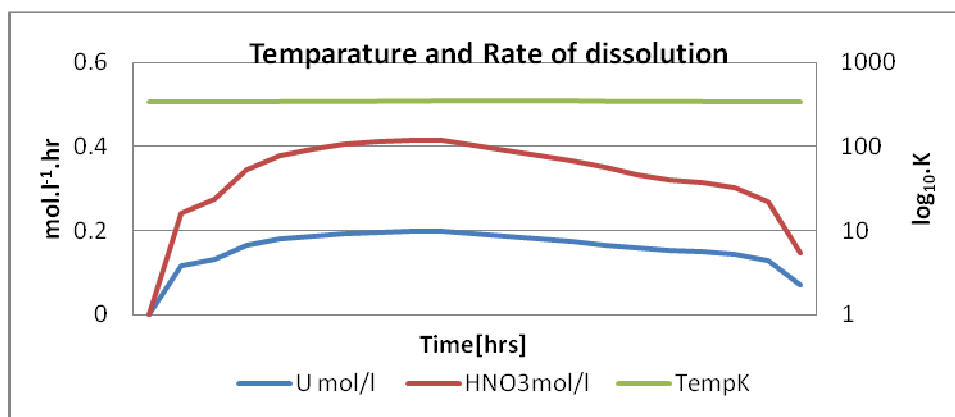
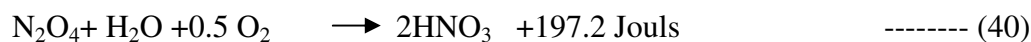


Figure 10: Rate of dissolution with triggering temperature 343K for unirradiated pellets

The heat of the reactions are given below;



## 6. GREEN CHEMISTRY AND OXIDATIVE DISSOLUTION:

The green chemistry is about environmental friendly design of chemical products and processes that reduce pollutant chemicals. It is governed by 12 basic principles given by Paul Anastas *etal*[25], of United States Environmental Protection Agency. This includes deploying the green solvents such as aqueous hydrogen peroxide for clean oxidants etc. There were many studies done in the scope of present paper to covert NO<sub>x</sub> in to nitric acid using hydrogen peroxide reviewed by W.L.Griffith *etal*.[26]. The present paper addresses the issue by employing the oxygen as depolarizing agent and acid as oxidizing agent for complete conversion of off-gases in to nitric acid. The objectives of green chemistry preventing effluent generation or waste generation, design for less or no production hazardous chemicals such as NO<sub>x</sub>, using renewable feed source such as regeneration of nitric acid, avoiding using of chemical derivatives, maximizing atom efficiency like less molar ratio of uranium to acid, increasing energy efficiency by avoiding steam usage, analyzing real time to prevent pollution by monitoring NO<sub>x</sub> in vent systems, temperature and pressure of the dissolver etc, minimizing the potential for accidents by incorporating auto excess pressure hydro releasing system and tertiary scrubbing system are well achieved in the present plant scale dissolution. The present study is real time plant scale study that is commercialized and operated through PLC based SCADA system for different types of raw materials.

## 7. CONCLUSION

The present study demonstrated dissolution reaction mechanism and reaction controlling ways with nitric acid flow rate and temperatures. The dissolution operating parameters such as

Maximum operable temperature, Initial temperature, Nitric acid flow rate and air flow rates for a 2MT plant scale batch were optimized.

1. It is found that the maximum operable dissolution temperatures is 85°C for Uranium octaoxide and 95°C for Uranium dioxide powders.
2. It is concluded that initial temperature to give the activation energy is 60°C in case of Uranium di oxide powders and 70°C in case of Uranium octaoxide powders.
3. It is observed that maintaining of nitric acid flow rate at 60lit/hr during first five hour period of reaction and subsequently 80lit/hr for the rest of the reaction is able to sustain the reaction within the maximum operable temperature.
4. It is also noticed that the changes in air flow rate has no significant effect on recovery of nitrous oxides during dissolution reaction.

## **8. ACKNOWLEDGEMENT**

Authors are very greatly indebted to control laboratory, quality assurance group, maintenance and ceramic fuel fabrication plants.

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