भुक्तशेष ईंधन का विघटन

4

भारतीय पीएचडब्ल्यूआर के लिए यूएनएफ के विघटन की दर का मूल्यांकन

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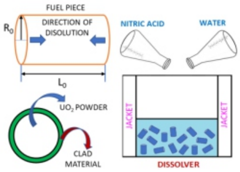

यूएनएफ के विशिष्ट कटे हुए ईंधन के टुकड़े और विलायक का योजनाबद्ध प्रदर्शन जहां कटे हुए टुकड़ों को पानी में गिराया जाता है और फिर कटे हुए ईंधन के विघटन के लिए सांद्रित नाइट्रिक अम्ल मिलाया जाता है।

सारांश

ईंधन पुनर्चक्रण का एक महत्वपूर्ण चरण प्रयुक्त नाभिकीय ईंधन (यूएनएफ) का विघटन है तथा अभिक्रिया की दर अभिकारक की सांद्रता एवं अभिक्रिया तापमान पर निर्भर करती है। भारतीय पीएचडब्ल्यूआर भुक्तशेष ईंधन हेतु अभिक्रिया दर की गणना करने के लिए सिकुड़ते कोर मॉडल (एससीएस) का उपयोग किया गया। इसके अलावा, विकिरणित पीएचडब्ल्यूआर ईंधन के अभिक्रिया दर की गणना हेतु वैज्ञानिक साहित्यों में बताए गए विभिन्न तरीकों का भी उपयोग किया गया। दरार की उपस्थिति में दर में काफी वृद्धि हुई है। वर्तमान विधि का उपयोग, तापीय एवं तीव्र रिएक्टर के किसी भी भुक्त ईंधन के विघटन की दर का मूल्यांकन करने के लिए किया जा सकता है।

Spent Fuel Dissolution

4

Evaluation of Rate of Dissolution of UNF for Indian PHWR

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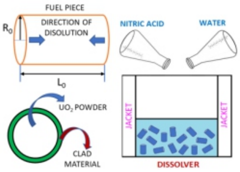

Schematic representation of typical chopped fuel piece of UNF and the dissolver where the chopped pieces are dropped into water and then concentrated nitric acid has been added for dissolution of chopped fuel.

ABSTRACT

The dissolution of used nuclear fuel (UNF) is a key step for fuel reprocessing and the rate of reaction depends on the reactant concentration and reaction temperature. Shrinking core model (SCM) is used to calculate the rate of reaction for Indian PHWR spent fuel. Further, the different methods reported in the literature are also applied to compute the rate of reaction for irradiated PHWR fuel. The rate is increased significantly in the presence of cracking. The present method can be used to evaluate the rate of dissolution for any spent fuel of thermal and fast reactor.

KEYWORDS: *Dissolution, UNF, PHWR, SCM, Fuel reprocessing*

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Introduction

India adopted close fuel cycle to utilize the resources efficiently and also to meet the increasing energy demand [1-2]. The spent fuel reprocessing [3-4] is bridging between 1st and 2nd stages of Indian Nuclear Power Program [5]. In this context, the reprocessing of used nuclear fuel (UNF) has immense importance to satisfy the close fuel cycle and also to reduce the high-active solid waste. So, the reprocessing of UNF from fast reactor also needs to place. Hence, the journey for UNF reprocessing from thermal to fast reactor, the major step is the efficient dissolution of UNF. In dissolution process, the chopped fuel is dissolved into concentrated nitric acid to obtain (Uranium and Plutonium) metal nitrate is formed. The rate of dissolution primarily depends on temperature and acid concentration. It has been found that the rate of dissolution is reduced with increasing plutonium content during the dissolution of mixed oxide (MOX) fuel [6-7]. Moreover, it is practically not possible to dissolve the MOX fuel in HNO_3 alone when PuO_2 increases beyond 35% by weight [8]. One has to introduce strong oxidizing agent to increase the dissolution rate [9-11]. So, the type of oxidizing agent has an important role in the rate of dissolution reaction. India has only commercialized the nuclear power production through thermal reactors. So, the reprocessing of UNF from thermal rector is only concerned in the present scenario to operate the fast reactor with MOX fuel which is a more attractive and wiser option for self-sustained power production.

The understanding of dissolution reaction is essential to design an efficient process. Several studies have been carried out in recent past to understand the mechanism of dissolution of various fuel compositions like UO_2, PuO_2 or MOX. Researchers carried out extensive studies to find out the role of various parameters like surface area, fuel content, HNO_3 concentration, temperature, mixing rate, size of pellet. Mineo et. al. proposed a simple rate equation for LWR spent fuel accounting the cracks formed during irradiation cycles and suggested that the initial effective dissolution area may increase in presence of cracks [12]. The HNO_3 penetration into the cracks was not considered. Further, Desigan et. al. investigated the effect of mixing rate and the rate of dissolution beyond 600 rpm shows negligible changes [13]. They also reported that the reaction is expected to be both diffusion and reaction controlled based on the estimated value of activation energy (E_a) as 26 kJ/mol. In general, if the $E_a > 40$ kJ/mol, then the rate is guided by chemical reaction & when $E_a < 20$ kJ/mol, it is diffusion controlled. Whereas E_a lies between 20 and 40 kJ/mol, signifies a mixed controlled regime [14]. A few studies also reported that the reaction mechanism may belong to both the transport and the surface controlled [15-16]. Additionally, Desigan et. al. observed that the rate is chemical controlled and the rate of reaction is increased with increasing initial HNO_3 concentration [17]. So, the evaluation of rate of dissolution for PHWR fuel has not been attended. Hence, the present studies have been carried out to calculate the rate of dissolution reaction of UNF for Indian PHWR.

Model and Methodology

The UNF containing 19 pins fuel bundles are chopped into pieces using gang chopper and the typical chopped pieces along with the dissolver are shown in Fig.1. The L_0 and R_0 define the initial length and initial radius of fuel piece. Here, the dissolution is considered as a semi–batch process where the HNO_3 is limiting reactant. The exothermic reaction for UO_2 fuel dissolution is as:

$$UO_2 + \frac{8}{3}HNO_3 \rightarrow UO_2(NO_3)_2 + \frac{3}{2}NO + \frac{4}{3}H_2O$$

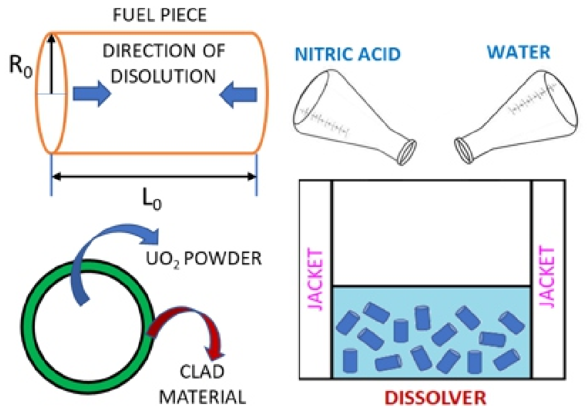

Fig.1: Schematic representation of typical chopped fuel piece of UNF and the dissolver where the chopped pieces are dropped into water and then concentrated nitric acid has been added for dissolution of chopped fuel.

The dissolution of UNF belongs to the domain of heterogeneous reaction where liquid and solid are reacted to produce liquid, solid and solid–liquid products. The behavior of solid–liquid interactions can be modelled using the shrinking core model (SCM) because the reaction takes place at the surface of the solid and the reaction zone moves into the solid core leaving behind the converted material. So, the SCM has been chosen to study the dissolution kinetics in HNO_3. The dissolution reaction can be expressed as

$$B\,(Solid) + n\,A\,(Liquid) \longrightarrow P\,(Liquid)$$

The heterogeneous reaction has been carried out through five steps (Levenspiel, 1972) [18]. **Step 1**: Diffusion of reactant A through liquid film surrounding the solid surface, **Step 2**: Diffusion of reactant A to the surface of unreacted core, **Step 3**: Reaction of liquid reactant A with the solid reactant B at the reaction surface, **Step 4**: Diffusion of the product P formed during reaction through to reach solid surface and **Step 5**: Diffusion of product through liquid film to reach bulk phase. The above reaction is either diffusion controlled or reaction controlled. If it is diffusion controlled then Steps 1, 2, 4 and 5 will be the rate determining steps whereas Step 3 will be the controlling step when it is reaction controlled. A schematic representation of the heterogeneous reaction is provided in Fig.2.

Further, the rate of reaction is directly proportional to the effective dissolution area and the rate equation can be expressed according to the stoichiometry of the reaction as

$$\frac{1}{S}\frac{dN_B}{dt} = \frac{1}{n}\,k\,C_A = k_L\,(C_{A0} - C_{AS}) \qquad (1)$$

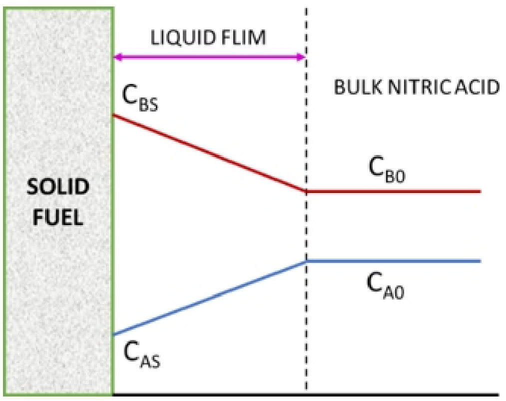

Fig.2: The schematic representation of the solid–liquid heterogeneous reaction with respective concentrations at solid surface at liquid film and at bulk liquid.

Where S denotes the dissolution area, N_B is the moles of solid B reacting at time t, n is the stoichiometric coefficient of liquid reactant A and k denotes rate constant. C_{A0} and C_{AS} are the concentration of liquid in the bulk and at the solid surface respectively. Here, the liquid–solid interaction is only possible through cross sectional area of the chopped fuel piece because the fuel has clad material (see Fig.1) and liquid is unable to access from axial side. Also, the acid attack through the pellet-clad gap has been neglected due to very narrow passage. So, the dissolution through axial direction is not considered here. Further, some assumptions have been made to solve the rate equation as: 1) The diffusion resistance of HNO_3 cannot be considered because no ash is formed on the surface of unreacted core. 2) The bulk resistance of reactant A is neglected under air sparging condition and 3) The diffusion resistance of product (metal nitrate) is also neglected under air sparging condition. Hence, the rate of reaction is only controlled by reaction and the reaction is pseudo-first order with respect to HNO_3. Design et al also suggested that the dissolution reaction is controlled by reaction in the temperature range of 233 – 363 K based on activation energy calculation [13]. Therefore, the rate equation (eqn. 1) can be solved by considering reaction controlled.

Now, the rate equation provided by Levenspiel is for spherical geometry [18]. So, the equations are modified according to the cylindrical geometry.

The eqn. (1) can be arranged based on C_{A0} is nearly equal to C_{AS}.

$$\frac{1}{(2\pi r^2)} \frac{dN_B}{dt} = \frac{1}{n} k\, C_A \tag{2}$$

As per the assumption of SCM, it can be written that

$$N_B = \rho_B V \text{ and } \frac{L_0}{R_0} = \frac{l}{r} = \delta \tag{3}$$

Where, ρ_B is the molar density of B in solid and V denotes its volume. The l and r are the length and radius of the shrinking particle at any given time and δ is the aspect ratio of the fuel piece at any instant. N_B can be rewritten in terms of r as

$$-dN_B = -3\pi \rho_B \delta r^2 dr \tag{4}$$

The rate of the reaction in terms of shrinking radius of the unreacted core can be expressed as

$$\frac{r}{R} = (1 - X_B)^{\frac{1}{3}} = 1 - \frac{2}{3} \frac{kC_B}{n\,\delta\,\rho_B\,R}\, t \tag{5}$$

The eqn. (5) denotes the rate equation for dissolution of fuel pieces with clad. X_B is the fraction of moles of reactant B that has reacted at time t. In another way, $(1–X_B)$ is the unreacted fraction of reactant B present at time t. The above equation can be arranged for the dissolution of UNF in nitric acid as.

$$\left(1 - \frac{[U]_t}{[U]_f}\right)^{\frac{1}{3}} = 1 - \frac{2}{3} \frac{kC_B}{n\,\delta\,\rho_B\,R}\, t \tag{6}$$

$[U]_t$ and $[U]_f$ are molar concentration of uranium at any time t and at the end of the dissolution reaction respectively. The rate constant of the dissolution reaction can be calculated from the slope of eqn. (6).

Further, the rate of dissolution reaction occurred at the fuel surface can be expressed as [12]:

$$\frac{dW}{dt} = W_0 \frac{d\beta}{dt} = a.IDR \tag{7}$$

Where, W signifies the dissolved weight of spent fuel, W_0 is the initial weight of U in the spent fuel. β denotes the fraction of dissolved fuel at time t and a is the effective dissolution area. IDR signifies the dissolution per unit area [12]. The effective dissolution area can be expressed as:

$$a = a_0\, F(\beta) \tag{8}$$

Where, a_0 denotes the initial effective dissolution area and F(β) is the ratio of effective dissolution area at a fraction of β to the initial effective dissolution area. It is worthy to find out the difference in effective dissolution area for unirradiated and irradiated fuels. It alters significantly from unirradiated fuel because the irradiated fuels have cracks which may affect the dissolution area. It is expected that a_0 can be increased in presence of cracks which finally influences the rate of reaction. The cracks may be present in radial and axial directions. The number of cracks and the angle between two cracks are the function of the rod power experienced in the reactor [12]. It has been assumed that the dissolution may occur in the axial and radial directions as indicated by arrows in the Fig.1. Now, the equation developed by Mineo et al. can be expressed as [12].

$$(1 - \beta)^{(1-p)} = 1 - (1-p)\frac{a_0}{W_0}\, k\, (C_H)^n\, t \tag{9}$$

So, the profile obtained by plotting a graph between $(1\text{-}\beta)^{(1\text{-}p)}$ and t is a straight line with an intercept 1.0. The rate constant of irradiated fuel can be evaluated from the slope of eqn. (9).

Experimental

In the present dissolution experiments, typical UNF from Indian PHWR (220 MWe) have been used. The physical characteristics of the fuel piece are given in Table 1.

The dissolution has been carried out in recirculation type SS dissolver for 100 fuel bundles and the experiment has been monitored through PLC/SCADA system. The air sparger in the

Table 1: Physical properties of chopped fuel piece.

Parameters	Value
Diameter of fuel pin (D), mm	14.47
Length of fuel piece (L), mm	40
Stoichiometric coefficient (n)	2.67
Molar density of B (ρ_B), gm/cc	10.5
Aspect Ratio (δ = L/R)	5.53

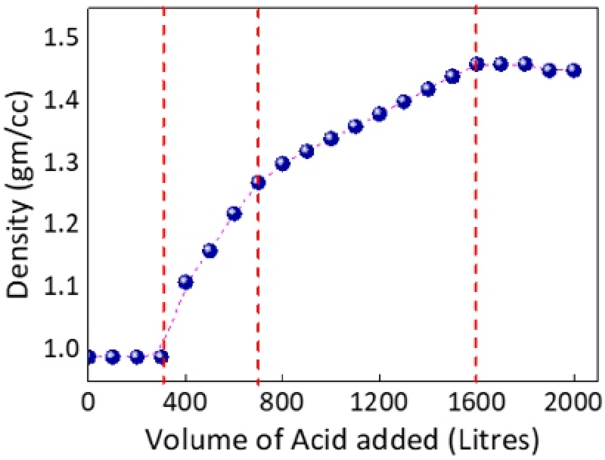

Fig.3: Density profile of spent fuel dissolution as a function of volume of 12M nitric acid.

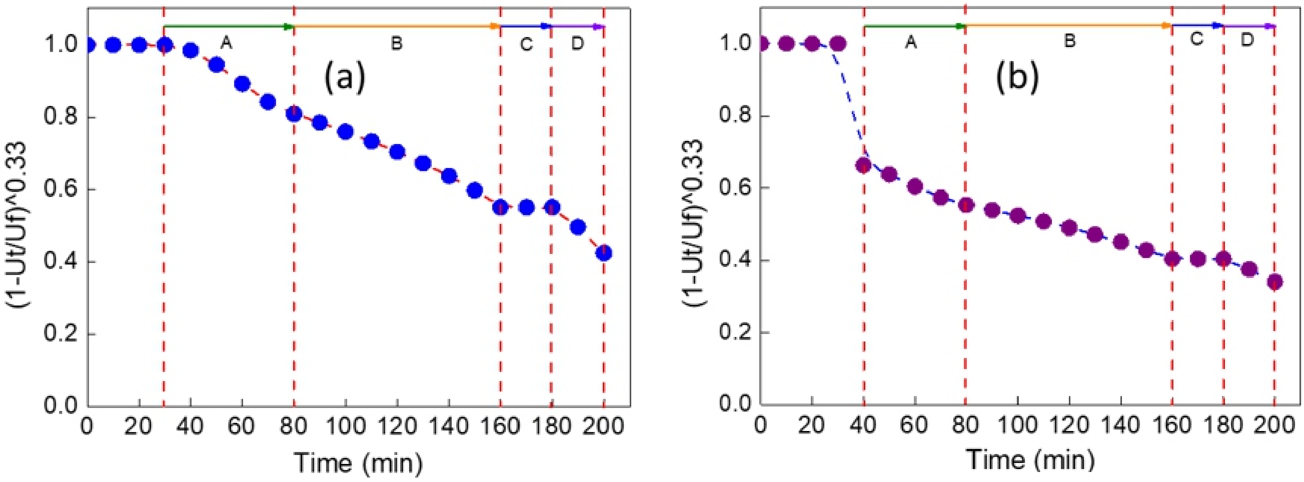

Fig.4: The Profile of [1 - ([U]t/[U]f)]$^{1/3}$ as a function of time (t) illustrating a decreasing trend (a) calculation based on uranium density in solution and (b) based on the solution density of uranyl nitrate.

dissolver has been kept on during the experiment for proper mixing of the dissolver content. The off-gas generated during the dissolver has been taken care in the off-gas treatment system. Initially the dissolver holds some volume of strip acid to reduce the impact of chopped fuel pieces. Then, the volume of 12M HNO_3 added in the dissolver is 2000 liters at a rate of 10 liter/min. The exothermic reaction has been started and continued till the temperature rises. No external heating or boiling has been carried out in the present experiment. The data has been collected from the SCADA system until the exothermic reaction is going on.

Results & Discussions

The dissolution reaction has been initiated after achieving a certain solution acidity. The density of U dissolved in nitric acid solution has been plotted against the volume of acid addition and an increasing trend is appeared (see Fig.3). It is obvious because the rate of reaction is proportional to the acidity of the solution. Further, it has been observed that the reaction is initiated after around 300 liters of acid addition and the overall acidity of the solution at that moment is approximately 2M. So, it is the minimum acid molarity required to start the exothermic reaction. Again, the slope is higher at initial stage because the rate of reaction is very high due to the high solid concentration. Then, the slope is comparatively lower because the increasing HNO_3 concentration and the decreasing solid concentration counter each other. Finally, the slope becomes flat which indicates the completion of exothermic reaction. The different zones based on variable slopes has been marked with vertical red dashed line. It has been noticed that the dissolution is achieved nearly 93%, not 100%. Because the rate of reaction is very slow due to low solid inventory and low overall acidity. The rate can only be increased by applying the external energy like heating or boiling which increases the temperature and also increases the rate constant. But in the present study, we are only interested to calculate the rate constant of exothermic reaction in absence of any external energy input.

So, the rate of reaction is varied with the time length of dissolution. According to the eqn. (6), the [1-([U]t/[U]f)]$^{1/3}$ has been computed from the experimental data and plotted against the time. The profile is displayed in Fig.4(a) and the rate of reaction can be evaluated from the slope of curve. The profile shows a decreasing trend with variable slopes and the various zones are marked with vertical red dashed line starting from Zone-A to Zone-D in Fig.4. The rate constant is obtained as 3.48x10^{-3} m/s using time average method. Further, the slopes have been calculated at different zones & it is ranging from -0.00269 to -0.00635. Then, the rate is appeared as 5.27x10^{-3} m/s using zone average method. So, the rate of dissolution obtained from time average method underestimates the rate obtained from zone average method. Next, the rate has been computed using the solution density of uranyl nitrate [see Fig.4(b)]. It has been found that the density is reflected after 30 minutes and a sudden fall in profile has been observed which is absent when the calculation has been carried out using uranium density. Here, the calculated rate is 2.67x10^{-3} m/s which underestimates the value obtained from uranium density. The rate obtained from zone average is 5.7x10-3 m/s which is in good agreement with the calculation using uranium density. The reported dissolution rate for UO_2 pellet at 70^{0}C is 3.08x10^{-3} m/s with initial nitric acid concentration of 10.28M [13]. It is obvious because higher concentration of HNO_3 (12M) has been used in the present study for dissolution. Hence, the zone average method is quite accurate for rate calculation.

In addition to that, the rate of reaction for irradiated UNF containing cracks has also been evaluated to find out the effect of cracks on the rate constant. The rate can be computed using eqn. (9) where the crack is considered in the radial direction. The inputs are provided in Table 2.

According to the eqn. (9), a profile has been generated when $(1-\beta)^{(1-p)}$ plotted as y-axis and t as x-axis using our experimental data for both the angles of 90^0 and 180^0 and it is displayed in Fig.5(a) and Fig.5(b) respectively. The trends are similar for both the angles. The rate of reaction has been calculated from the slope of the curve using zone average method and they are 4.1x10^{-2} m/s for 90^0 and 3.1x10^{-2} m/s for 180^0. The rate of dissolution is quite high in the presence of cracks and it is around 10 times higher compared to that of the non-cracking condition. But there is no significant change in

Table 2: Inputs for irradiated fuel.

Parameters	Value
a_o (m^2)	22.73 x 10^{-6}
W_o (gm)	64
p	0.4896 (θ = 90^0) 0.3352 (θ = 180^0)
Temperature (T), K	333
Conc. of HNO_3 (C_H), M	6.5
n	2.67

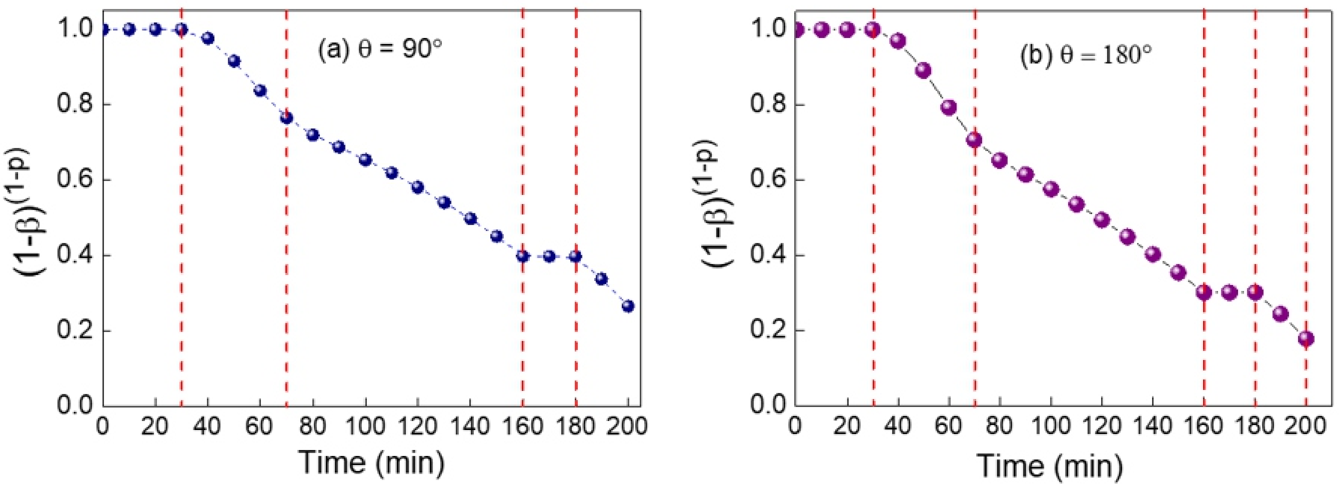

Fig.5: The Profile of $[1 - ([U]t/[U]f)]^{1/3}$ as a function of time (t) illustrating a decreasing trend (a) calculation based on θ = 90^0 and (b) based on θ = 180^0.

Table 3: Rate of dissolution calculated using three models in presence of cracking and rate of dissolution evaluated in present study.

Rate of Dissolution (m/s)	Method	Ohsaki Model	Fukasawa Model	Nemoto Model	Present Study
(θ = 90)	Time average	0.062	0.014	0.101	0.018
	Zone average	0.124	0.033	0.190	0.041
(θ = 180)	Time average	0.073	0.016	0.119	0.021
	Zone average	0.095	0.025	0.146	0.031

the rate of reaction for 90^0 and 180^0. So, it can be stated that the rate of dissolution has negligible dependency on the angle between cracks. It can be noted that the rate calculation using zone average method is more accurate.

Further, Mineo et al reported various prescription to calculate the rate of dissolution reaction based on temperature and nitric acid concentrations [12]. So, the rate has been computed using all the models proposed by Ohsaki et al [19], Fukasawa et al [20] and Nemoto et al [21] and displayed in Table 3. The rate of dissolution predicted by Ohsaki and Nemoto is overestimating the rate calculated from the experiment whereas Fukasawa model is in good agreement with the present study. Because the stoichiometry of the reaction considered by Fukasawa et al converges to our experimental studies. The stoichiometric ratio for other models is comparatively low which leads to a high rate of dissolution reaction.

Conclusions

The rate of dissolution reaction has been computed for UNF of Indian PHWR using shrinking core model (SCM) and found the rate of reaction is in the range of $5.27x10^{-3}$ to $5.70x10^{-3}$ m/s using zone average method. The calculated rate of reaction obtained from experiment is in well agreement with the reported value. The zone average method is quite promising for calculation of rate of reaction. Further, the rate of reaction for irradiated fuel has been improved in presence of cracks and the rate is obtained in the range of $3.1x10^{-2}$ to $4.1x10^{-2}$ m/s. Hence, the present methodology can be applied to calculate the rate of reaction for the dissolution of fast reactor used nuclear fuel during reprocessing.

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