Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.808804

52 (2014) 490–497
January

Taylor & Francis
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Dissolution kinetics of zirconium dioxide in nitric acid

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Received 6 March 2012; Accepted 14 March 2013

ABSTRACT

Dissolution kinetics of zirconium dioxide (ZrO_2) in nitric acid was investigated as a function of time, temperature, acid concentration, stirring speed, solid to liquid ratio, and surface area. The dissolution appears to be a two-stage dissolution process that is related to the changes at the solid surface; the outer layer being more susceptible to dissolution than the inner layer. The initial rate of ZrO_2 dissolution was used for the comparison studies. The dissolution of zirconium dioxide follows a pseudo-first-order rate equation. An increase in the temperature of the dissolving medium enhances the initial dissolution rate of the ZrO_2. The activation energy was found to be 43.3 kJ/mol. A probable dissolution mechanism consistent with the experimental data is suggested and the steps involved in the reaction are discussed. The results are explained in terms of a surface reaction mechanism. The effect of ultrasound on the rate of zirconium dioxide dissolution was also investigated.

Keywords: Dissolution rate; Kinetics; Zirconium dioxide; Nitric acid; Ultrasound; Activation energy

1. Introduction

Dissolution of metal oxides is of considerable practical importance in fields like extraction of valuable metals from ores, transport of metal in hydrologic cycles, and the removal of oxide deposits from metal surfaces [1] i.e. in metallurgy, ceramic science, and geology [2]. ZrO_2 exists as monoclinic crystals at room temperature and it transforms to tetragonal and cubic structure as the temperature increases. It has low thermal conductivity (23 W/m.K), hence it can be used as thermal barrier coating in jet and diesel engines to allow high-temperature operations. Stabilized zirconium dioxide (zirconia) is used in oxygen sensors and fuel cell membranes because it has the ability to allow oxygen ions to move freely through crystal structure at higher temperature. Zirconium is not found as a free metal, but principally in the zirconium silicate ($ZrSiO_4$) form. The oxide baddeleyite (ZrO_2) is among many minerals that contain zirconium. Zirconium compounds possess useful properties which have been utilized for various applications. Zirconium has many advantages over other transition

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Presented at the DAE—BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology (SESTEC 2012) Mumbai, India, 27 February–1 March 2012

metals, and was found to be the best metal for nuclear reactors and submarines. Zirconium does not corrode at high temperature because it forms a stable protective passive oxide film. Zirconium alloys (zircaloys) are also used to make cladding for the uranium oxide fuel elements. Zircaloys are favored over stainless steel cladding because they have lower neutron cross section, appropriate thermal conductivity, and both corrosion and mechanical resistances [3].

Zirconium metal has an oxidized surface which provides resistance to the chemical attack, making it ideal not only for chemical plants but also for body implants such as hip replacement joints. One of the problems associated with using zirconium alloys as cladding for nuclear (uranium oxide) fuel rod is hydride-induced embrittlement which results in the corrosion of zircaloys. At high temperatures occurring in nuclear reactors, hydrogen is produced by reaction of coolant water with zirconium. The hydrogen in turn can diffuse into the zircaloy cladding to produce hydrides. The hydrides are a brittle phase which has a considerable impact on the mechanical properties of cladding materials [3].

The dissolution of zirconium dioxide with concentrated nitric acid alone is not studied sufficiently. Most of the dissolution experiments were studied with the combination of acids; for example, pickling with nitric-hydrofluoric acid [4]. The main reason behind this is zirconium and to a lesser extent its alloys, are resistant to a wide range of acidic and alkaline solutions, with the exception of hydrofluoric acid [5]. Dissolution studies were carried out with a mixture of concentrated nitric acid and dilute hydrofluoric acid [4]. Irradiated zirconium coupons were used for the dissolution in which gradual decrease in the area of coupon takes place as the experiment proceeds. The rate of dissolution of zirconium metal is first order with respect to HF. It was observed that there is only a small change in the rate of dissolution with nitric acid which indicates that during dissolution ZrO_2 is not directly attacked by nitric acid, but presence of nitric acid helps in regeneration of HF. However, the presence of 13 M nitric acid produces a stable solution. The value of energy of activation indicates the process to be transport controlled (26.78 kJ/mol). The reactivity of the surface of zirconium during pickling by nitric-hydrofluoric acid was studied [6]. In this work, the behavior of zirconium in HF-HNO_3 pickling solution acid was studied by using electrochemical methods, X-ray diffraction, and Raman spectroscopy. It was again observed that the zirconium dissolution rate depends only on hydrofluoric acid concentration. Dissolution kinetics of TiO_2 in HF-HCl solution has also been studied as a function of time, temperature, and acid concentration [2]. They have also shown that the rate of dissolution is independent of HCl concentration and depends only on the concentration of HF. The kinetics is studied by assuming the rate to be chemical reaction controlled by applying shrinking core model. This system also exhibits exponential temperature dependence with activation energy of 74.9 kJ/mol; in all these cases, the rate was found to be first order with HF.

The leaching of uranium has been studied under conventional stirring method and also by using ultrasound [7]. The enhancement in the rate of ultrasound-assisted leaching is higher when nitric acid concentration is low and sulfuric acid concentration is high. The kinetics of this system was represented by classical shrinking core mode assuming that the surface reaction is fast and diffusion from ore particle is the rate controlling step.

In the present study, dissolution was carried out at various concentrations of nitric acid (HNO_3). It appears that the zirconium dioxide does not directly dissolve into HNO_3 but it first transforms to its salt zirconyl oxynitrate ($ZrO(NO_3)_2$) by chemical reaction and then the salt gets dissolved into aqueous HNO_3. The possible chemical reaction is:

$$ZrO_2 + 2HNO_3 \rightarrow ZrO(NO_3)_2 + H_2O \tag{1}$$

The dissolution was studied and the optimization of the parameters in a conventional agitation method was carried out and a kinetic model for enhancement of dissolution of ZrO_2 is proposed. Many papers have been published on the kinetics of the dissolution of the metal system and many have also proposed the kinetic model which fit their observation. If a model corresponds closely to what really takes place, then its rate expression will closely predict and describe the actual kinetics; if a model widely differs from reality, then its kinetic expression will be useless [8].

2. Materials and methods

The materials used for experiments were LR grade zirconium dioxide which had assay of 99.0% based on ignited substances obtained from Thomas Baker. Nitric acid (AR grade) with an assay of 70% and specific gravity of 1.42 used for dissolution experiments was obtained from S.D. fine Chemicals Limited, India. Distilled water has been used for all the experiments in the preparation of different concentrations of nitric acid solutions. Boric acid (extra pure) and sodium hydroxide pellets (AR Grade) of S.D. Fine Chemicals Limited were used for the preparation of borate buffer. 4-(2-Pyridylazo) resorcinol monosodium salt (PAR) indicator having molecular formula $C_{11}H_8N_3NaO_2 \cdot H_2O$ (molecular weight 255.21) was used as complexing agent for estimation of zirconium ion present in the solution.

2.1. Powder characterization

Zirconium dioxide used in the dissolution experiments was a commercially available powder. The ZrO_2 powder was agglomerated with an agglomeration size distribution shown in Fig. 1 as obtained using a particle size analyzer. The volume average diameter was found to be 5.34 μm. The images were captured by LEICA GALEN III microscope as shown in Fig. 2. The results of BET gas adsorption on the same powder gave an average specific surface area of $14.6\,m^2/g$ ($82.9\,m^2/cm^3$). The mean volume crystal diameter was found to be 0.073 μm.

2.2. Dissolution experiments

Experiments were performed in $0.35\,dm^3$ three-neck cylindrical-shape round bottom glass reactor. The glass reactor used for dissolution studies had three valves: one for sampling, one for condenser, and the one for thermocouple to monitor the temperature of the process. A six-bladed glass impeller was used and this resulted in suspending the solids satisfactorily. The agitation speed was varied using a variable speed drive motor between 200 and 2000 rpm. In $0.25\,dm^3$ nitric acid solution, 3 g of ZrO_2 powder was suspended. The speed of agitation was kept at 600 rpm in most of the experiments. Experiments were also carried out at different temperatures. The dissolution experiments performed had the total reaction time of 6 h and more than 6 h in some cases. Aliquots of reaction mixtures were removed using a 5 ml pipette, at intervals with time gap of 30 min and 1 h in some cases, till 6 h of reaction completion. These samples were then filtered by filter paper to remove suspended particles if any. With this procedure, 10–15 samples were collected for analysis. Analysis of the collected samples was done by using UV–visible spectrophotometer at the wavelength of 530 nm.

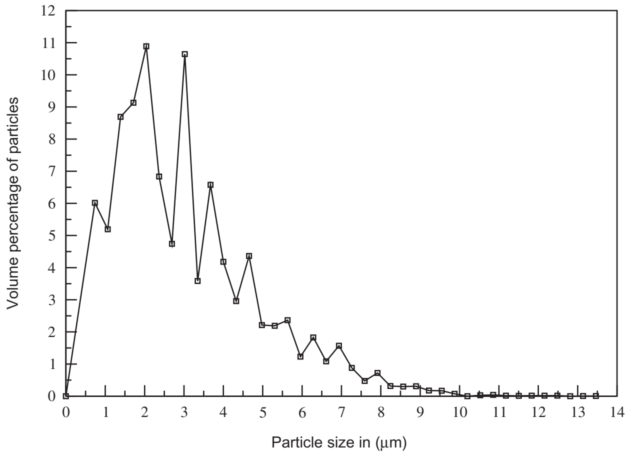


Fig. 1. Size distribution of initial ZrO_2 powder.

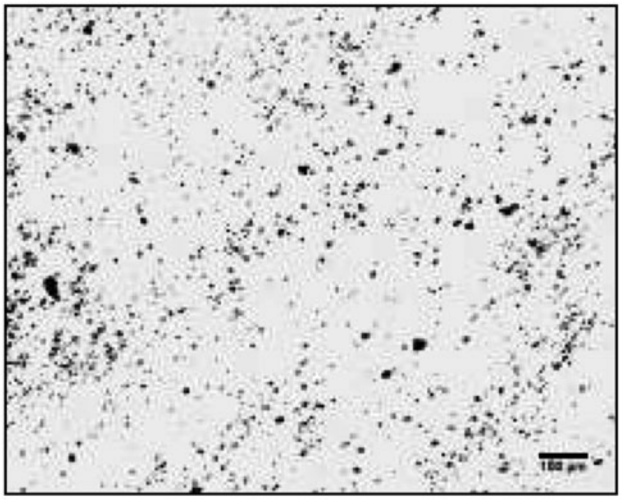


Fig. 2. Microscope image of initial ZrO_2 powder.

2.3. Analysis procedure

(1) *4-(2-Pyridylazo)resorcinol (PAR) solution*: A 0.1% (w/v) solution was prepared by dissolving the appropriate quantity in distilled water.
(2) *Borate buffer*: A sodium borate buffer solution was prepared by keeping the sodium hydroxide to boric acid weight ratio 1:2.

Aliquots (1 ml) of the concentrated samples were added to 1 ml of reagent solution (PAR Solution). The pH of the solution was adjusted to 6.3 with borate buffer. The solution was made up to 25 ml in a volumetric flask with water. The zirconium complex was measured at 530 nm [9] using Agilent 8453 UV–visible spectrophotometer. Sensitivity of the analysis was ±1%. All the analyses were carried out at room temperature of 25 ± 2°C.

3. Results

Dissolution experiments were carried out with washed zirconia i.e. pre-washed multiple times with distilled water to determine and eliminate, if any, salts of zirconium as an impurity. Similar rate of dissolution was observed in both the cases indicating the absence of any water soluble impurity in powder. The initial dissolution rates for the experiments were determined from the initial linear portion of each curve by a linear regression analysis. The specific dissolution rate is represented as g of Zr ion dissolved per m^2/s.

3.1. *Role of surface area*

Scanning electron microscopy (SEM) analysis of ZrO_2 powder was done before and after reaction, the images obtained were used to study the change caused by acid on surface. Fig. 3 shows SEM of ZrO_2 powder after 6 h in 10 N HNO_3 at 90℃ and 600 rpm. The agglomerate of the partially dissolved powder showed surface etching in comparison to the agglomerate in the powder before reaction as shown in Fig. 3.

Effect of surface area (coarse and fine powder) and solid loading on rate of ZrO_2 dissolution was investigated. Fig. 4 shows the change in volumetric rate of dissolution as a function of solid loading (weight of solid/volume of liquid). Fig. 5 shows the comparison between the fine and coarse powder dissolution rate. ZrO_2 powder of surface area 14.6 m^2/g was sieved to segregate coarse powder whose surface area was estimated to be 12.1 m^2/g and the remaining fine powder was further grounded into even more finer size whose surface area was estimated to be 19.6 m^2/g by BET.

According to the experimental results presented, it was observed that the initial dissolution rate is proportional to the surface area.

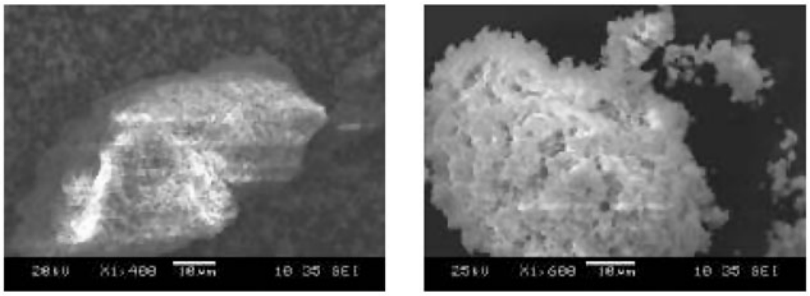
3.2. *Effect of acid concentration*

Dissolution rate for ZrO_2 in HNO_3 at concentrations ranging from 1 to 15.8 N at 90℃ and 600 rpm is shown in Fig. 6. The initial dissolution rates were determined from the initial linear portion of each curve as described above. The optimum concentration of acid for the dissolution and its effect on dissolution rate was estimated from this study. The observed results showed that initial rate of dissolution increases with nitric acid concentration from 1 to 5 N and above that it remains nearly constant. Since there was no significant change in the rate when the concentration of nitric acid was above 5 N as shown in Fig. 7, further studies were carried out at 10 N nitric acid concentration. At 10 N nitric acid concentration, any slight change in strength of nitric acid would not have significant effect on initial rate of dissolution. Reduction in dissolution rate of ZrO_2 was observed at every concentration of acid studied once the dissolved Zr ion concentration reaches a particular concentration above which the dissolution rate reduces significantly.

3.3. *Temperature dependence*

Temperature dependence of ZrO_2 dissolution in 10 N HNO_3 at 600 rpm is shown in Fig. 8. Dissolution rates were taken as the slopes of the regression lines that were fitted to the initial linear portion of each curve. The dissolution study indicated steady rise in dissolution rate at lower temperature i.e. at 30 and 60℃ at stipulated time of reaction. At higher temperature i.e. at 90℃, the initial rise in the rate changes into sluggish rate culminating into a plateau.

The reaction was conducted for extended period at lower temperature (i.e. at 60℃) to verify any similarities in alteration of rate as obtained at 90℃. The study showed that the alteration in dissolution rate is delayed at lower temperature and is observed once the dissolved Zr ion concentration reaches a particular value (i.e. ~20 ppm). The dissolution rates and temperature curves for each rate are listed in Table 1. The dissolution rates as a function of temperature are plotted in Fig. 9 and apparent activation energy of 43.3 kJ/mol is obtained.



Before reaction **After reaction**

Fig. 3. SEM examination of ZrO_2 powder before and after dissolution in 10 N nitric acid at 90℃ and 600 rpm for 6 h.

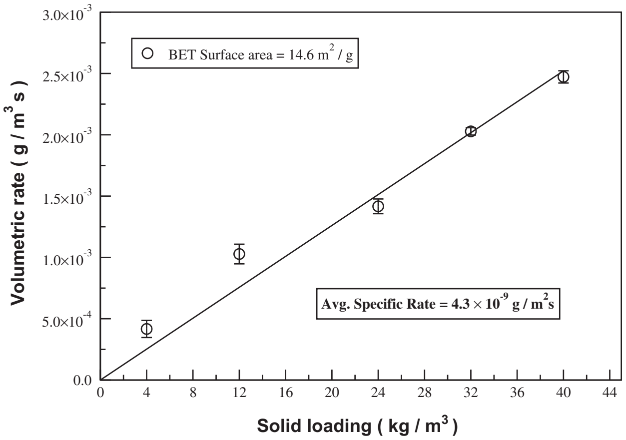


Fig. 4. Effect of solid loading on dissolution kinetics at 60°C.

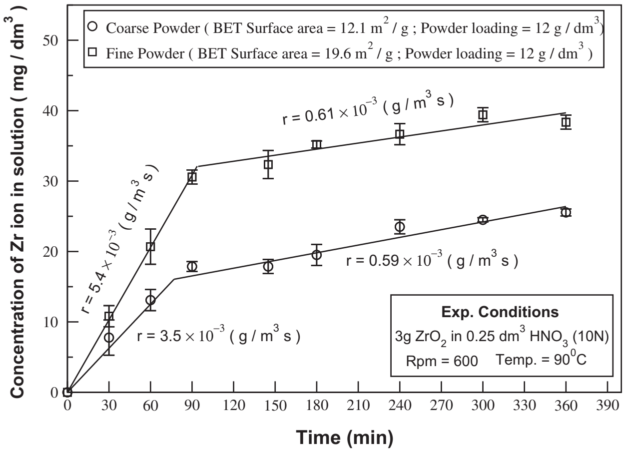


Fig. 5. Effect of surface area on the rate of dissolution.

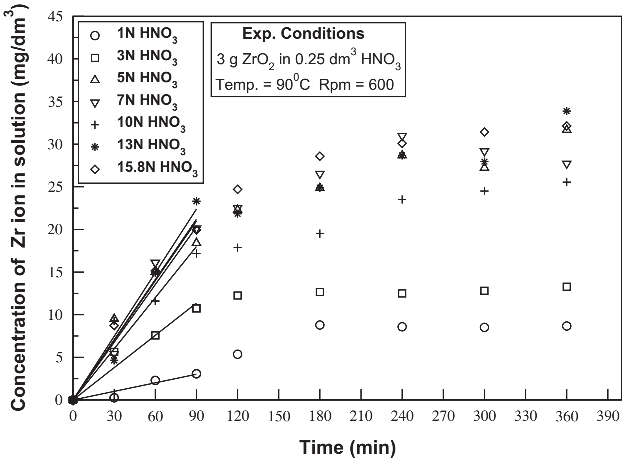


Fig. 6. Effect of HNO_3 concentration on dissolution kinetics at 90°C.

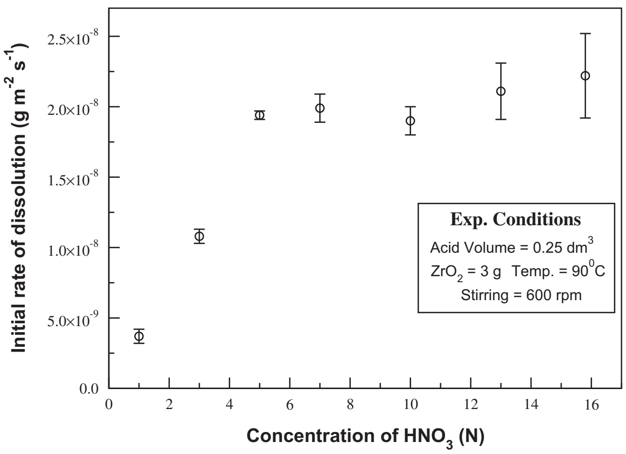


Fig. 7. Variation in the initial rate of dissolution by varying HNO_3 concentration, measured at 90°C.

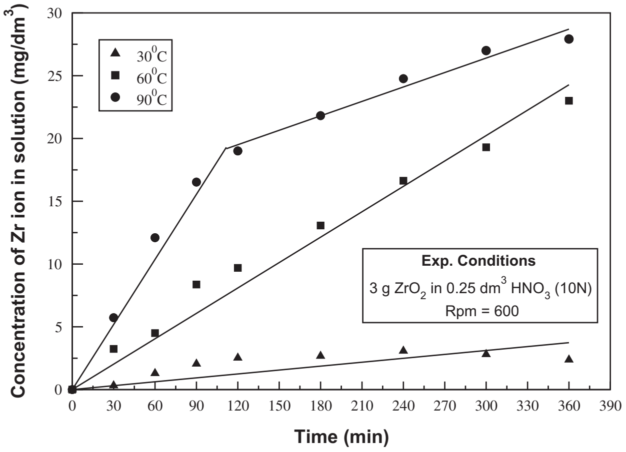


Fig. 8. Effect of temperature on dissolution kinetics in 10 N HNO_3.

3.4. Possible causes for reduction in dissolution rate

It was observed that dissolution rate is higher initially and after some time, the rate becomes sluggish. To investigate the cause for such behavior, the ZrO_2 powder already used once for dissolution study was taken and was reused for another experiment in fresh acid. Similarly, the used acid for dissolution was reused with fresh powder for dissolution. It was

Table 1
Effect of temperature on dissolution rate

Temperature (K)	Rate ($g\,m^{-2}s^{-1}$)
303.15	$1.0 \pm 0.05 \times 10^{-9}$
333.15	$6.3 \pm 0.5 \times 10^{-9}$
363.15	$16.5 \pm 1.4 \times 10^{-9}$

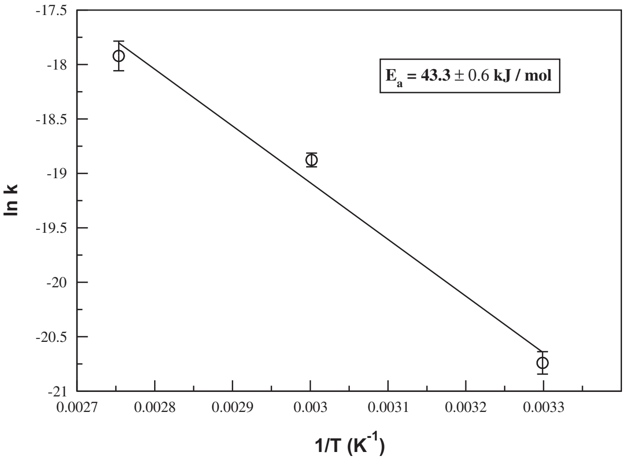


Fig. 9. Log (rate of dissolution) vs. inverse temperature to determine the apparent activation energy for the dissolution kinetics.

observed from the results as shown in Fig. 10 that the dissolution rate of fresh powder and fresh acid was almost similar to reused acid, whereas for reused powder the rate is significantly lower. Hence, it can be concluded that slowing down of reaction rate (i.e. sluggish rate) cannot be attributed to any change in liquid phase i.e. nitric acid. The reduction in reused solid dissolution rate indicates that sluggish reaction rate observed in the earlier experiments is due to surface changes.

3.5. Effect of stirring

Experiments have been performed using conventional stirring process. Rotational speeds of the impeller were maintained at 200, 400, 600, 1300, and 2000 rpm in 10 N HNO_3 and 60˚C. The effect of stirring on dissolution rate of zirconium has been represented in Table 2. It can be observed from Table 2 that the increase in energy input by conventional stirring does not exhibit much improvement beyond 600 rpm. Visual observation indicates that the powder is well suspended at 200 rpm. The low dissolution rate of ZrO_2 indicates that the mass transfer resistance will be almost negligible in the present study. However, rpm of 600 was kept to ensure particle suspension.

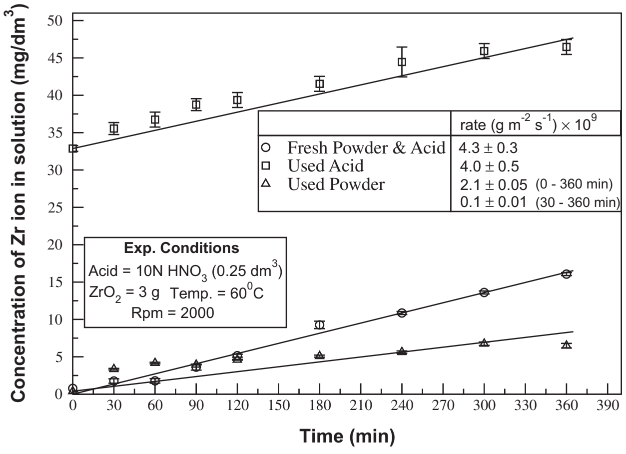


Fig. 10. Investigation on the sluggish rate observed in the dissolution experiment showing reduction in dissolution rate for used zirconia powder.

3.6. Effect of ultrasound

Ultrasound can produce high temperature and high pressure micro jets which can contribute significantly in the dissolution rate [10]. Considering the advantages of ultrasound, the dissolution studies were carried out in 10 N HNO_3 at 60˚C without stirring. The ultrasound bath used for the study was of frequency 36 kHz and had power of 27 W/L. The observed dissolution rate was compared with the conventional method measured in 10 N HNO_3 at 60˚C and at 1,300 rpm. The initial dissolution rate obtained from this study was observed to increase significantly as shown in Fig. 11. Use of ultrasound enhances the initial dissolution rate nearly three times than the conventional method. Ultrasound vibrations can cause, along with other effects, a decrease in the diffusion layer thickness and thus an increase in the initial rate.

Since in the present study the powder used is not poly-dispersed, the variation observed in dissolution rates is not due to the disappearance of fine particles. The sluggish rate is possibly due to the change that occurs on the particle surface during the dissolution of ZrO_2.

4. Discussion

4.1. Dissolution kinetics

The dissolution curve determined in this study shows dissolution of monoagglomerated and monodispersed powders controlled by a surface reaction [11],

Table 2
Effect of agitation on rate of dissolution

Rpm	Initial rate ($g\,m^{-2}\,s^{-1}$)
200	$4.9 \pm 0.2 \times 10^{-9}$
400	$5.2 \pm 0.2 \times 10^{-9}$
600	$5.9 \pm 0.3 \times 10^{-9}$
1300	$3.7 \pm 0.2 \times 10^{-9}$
2000	$3.8 \pm 0.3 \times 10^{-9}$

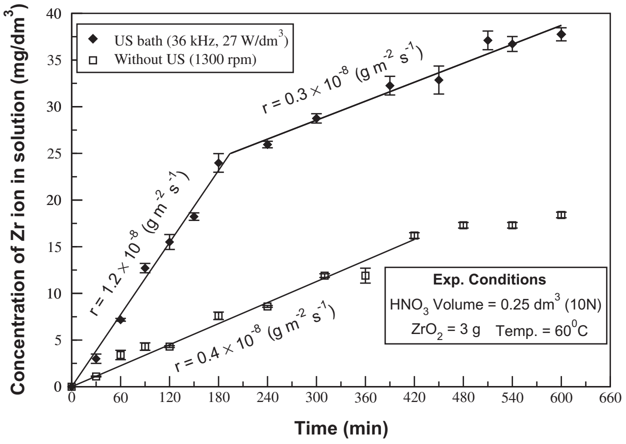


Fig. 11. Effect of ultrasound (US) on rate of dissolution.

$$1 - (1 - f)^{1/3} = kt/d_0$$

where f is the fraction reacted, k is a rate constant, t is time, and d_0 is the initial particle diameter. The dissolution curves are characterized by an essential linear region up to about 20 mg/dm^3.

The dissolution curve in Fig. 5 shows that surface area has a significant effect on ZrO_2 dissolution rate. The order of reaction is pseudo-first-order with respect to ZrO_2 loading. The dissolution rate dependence on temperature yields activation energy of 43.3 kJ/mol. The ZrO_2 dissolution reaction has a weak dependence on the HNO_3 concentrations. There is an increase in rate at lower concentrations of nitric acid, while at higher concentrations the rate of dissolution almost remains constant.

The possible rate-limiting mechanism for the ZrO_2 and nitric acid reactions can be represented into three progressive steps. Initially, the diffusion of nitric acid from bulk phase to the surface of the ZrO_2. Reaction on the surface between nitric acid and ZrO_2 would be the second step and finally, the diffusion of product from the surface of the ZrO_2.

4.2. Mechanism for ZrO_2 dissolution

4.2.1. Shrinking core model

Shrinking core model is best fit for most of the heterogeneous systems due to its compatibility with real conditions more closely than progressive conversion model or any other model. The present system has very low conversion of zirconium dioxide. The reason behind the low conversion of zirconium dioxide is its resistance to most of the acids and bases except hydrofluoric acid and the present system uses nitric acid for the dissolution studies. Due to low conversion of reactant, the particle size reduction at the end will be very little. Hence, the radius of particle remains almost the same till the end of the reaction.

The shrinking core model is applicable when complete converted material is obtained with unchanged particle size at the end of reaction or the solid particle itself shrinks and disappears at the end of reaction [8]. However, none of the above is satisfied by present system, so shrinking core model cannot be applied to present system. Hence, other conditions of experimental results were investigated to develop the kinetics of the proposed system.

4.2.2. Role of diffusion

Liquid–solid heterogeneous reactions that are generally controlled by diffusion processes have the activation energy (E_a) values ranging between 10 kJ/mol and 20 kJ/mol [12]. However, in the present system, the order of reaction is pseudo-first-order with respect to zirconium dioxide, and the activation energy is 43.3 kJ/mol.

In summary, the concentration dependence, the temperature dependence, and the mass transfer resistance estimates show that the rate of dissolution is not affected by diffusion resistance. Therefore, some surface reaction mechanism needs to be established.

5. Conclusions

Zirconium dioxide in nitric acid had very low rate of dissolution. The sluggish rate observed in dissolution curve is possibly due to modification on the solid surface. In nitric acid, the rate of dissolution of zirconium dioxide is pseudo-first-order with respect to zirconium dioxide. The initial rate of dissolution does not change significantly above 5 N nitric acid concentration. Increase in surface area, either by decreasing the particle size or by increasing the surface area per unit volume, increases the dissolution rate. Stirring has no significant improvement in the initial rate of dissolution suggesting no mass transfer limitations. The activation energy for the dissolution of zirconium dioxide in nitric acid is 43.3 kJ/mol for the temperature ranges 30–90˚C. Use of ultrasound increases the initial rate of dissolution significantly. The value of energy of activation suggests that the dissolution rate is chemical-reaction controlled.

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