

STUDIES ON THE KINETICS OF  $UO_2$  DISSOLUTION IN CARBONATE-  
BICARBONATE MEDIUM USING SODIUM HYPOCHLORITE AS OXIDANT

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Received 5 August 1996

Accepted 16 August 1996

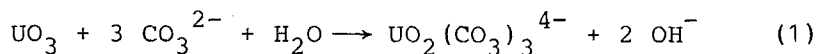
The dissolution of  $UO_2$  in carbonate-bicarbonate solutions containing sodium hypochlorite as an oxidant has been investigated. The effect of temperature, sodium hypochlorite concentration and stirring speed was examined. In the temperature range of 303 to 318 K, the leaching reaction displayed linear kinetics. Apparent activation energy obtained from the differential approach was found to be 57 kJ mol<sup>-1</sup>. This relatively high activation energy value indicates a chemically controlled behavior of  $UO_2$  dissolution. The order of reaction with respect to sodium hypochlorite concentration was found to be unity.

## INTRODUCTION

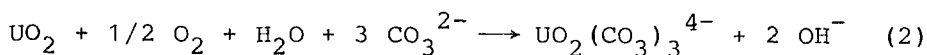
Sulfuric acid leaching is the most widely practiced process to extract uranium from the uranium-bearing ore bodies. However, not all deposits of uranium may be amenable to acid leaching due to the presence of acid consuming gangue materials. Alkaline leaching is there-

fore the recommended leaching technique for recovering uranium from such ores. Sodium carbonate-sodium bicarbonate solution is the common lixiciant in the alkaline leaching route for ores containing uranium both in hexavalent and tetravalent states. While hexavalent uranium readily dissolves in carbonate medium, tetravalent uranium being insoluble, needs to be oxidized by incorporating a suitable oxidizing agent in the leaching medium.

The oxidation of U<sup>4+</sup> to U<sup>6+</sup> in the sulfuric acid leaching system has been extensively studied in the past<sup>15</sup>. Manganese dioxide, KClO<sub>3</sub>, Fe<sup>3+</sup> and atmospheric oxygen are the most common oxidizing agents for leaching in acidic medium. Hydrogen peroxide has also been used by some researchers<sup>6</sup>. Sodium carbonate-sodium bicarbonate and ammonia-ammonium carbonate are the most important lixivants for the alkaline leaching of both U<sup>4+</sup> and U<sup>6+</sup> present in the ores. Hexavalent uranium oxide undergoes non-oxidative dissolution in carbonate solution forming a tricarbonatodioxouranate(VI) complex, as shown in the reaction



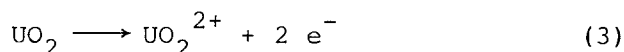
The dissolution of UO<sub>2</sub> is characterized by the following overall reaction in the presence of oxygen as oxidizing agent:



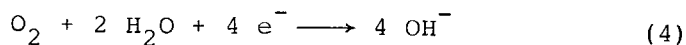
The pH of the solution is maintained below 10 by adding bicarbonate ions to prevent the precipitation of uranate(VI) salt. Many investigators have studied the kinetics of UO<sub>2</sub> dissolution in carbonate solution<sup>7-9</sup> in the presence of oxygen. Earlier it was believed that the

surface diffusion of dissociated oxygen atoms resulted in the conversion of UO<sub>2</sub> to UO<sub>3</sub>, which however failed to consider the electrochemical nature of UO<sub>2</sub> dissolution. This was a drawback in describing the actual mechanism of the leaching process. Habashi and Thurston<sup>3</sup> suggested that the dissolution of UO<sub>2</sub> in the presence of an oxidant in both acidic and alkaline medium occurred by an electrochemical mechanism, which overcomes some of the inherent difficulties of the previous diffusion theory. The electrochemical character of uranium extraction was analyzed in terms of two half-cell reactions.

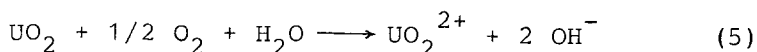
The anodic dissolution of UO<sub>2</sub> is represented by



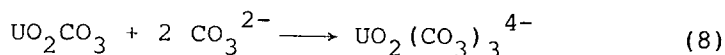
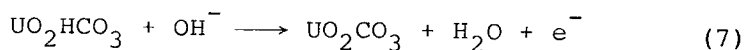
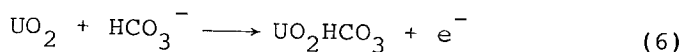
and the cathodic reduction of oxygen occurs according to



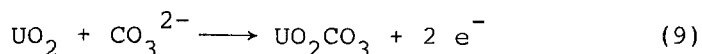
The net reaction can be written as



Even though the most accepted theory failed to analyze the kinetics in terms of rate-determining charge transfer steps, Nicol and Needes<sup>10-11</sup> developed a charge transfer mechanism of the electrochemical leaching process. Based on their kinetic data they proposed the following scheme of reactions:



The same authors in their subsequent publication<sup>12</sup> proposed a charge transfer mechanism, in which a single two electron process replaces one electron steps:



As the leaching follows an electrochemical mechanism, theoretically the cathodic reaction can be affected by any oxidizing system that has a standard potential such that the sum of two half-cell potentials would be positive. However, the choice of oxidant must depend on its effect on the U extraction process, on the environment and also on the economy of its use.

The literature on extractive metallurgy shows that sodium hypochlorite has been used as an oxidant for leaching of uranium and molybdenum ores<sup>13-14</sup>. These experiments were conducted in order to find the most suitable oxidant for tetravalent uranium, but a detailed kinetic study of uranium extraction by hypochlorite as an oxidant has not been reported. The present study was, therefore, undertaken to investigate the kinetics and mechanism involved in the dissolution of  $\text{UO}_2$  by sodium hypochlorite as an oxidizing agent in carbonate-bicarbonate medium.

## EXPERIMENTAL

High purity uranium dioxide powder with an O:U ratio of 2.2 and average particle size of 50  $\mu\text{m}$  was used for all leaching experiments. Reagent grade chemicals were used throughout the investigation.

Leaching studies were carried out in a magnetically stirred 0.5 l batch reactor kept inside a thermostat. For each test the reactor was charged with 100 ml solu-

tion of 0.5M total carbonate-bicarbonate concentration and equilibrated to a desired temperature, before adding 0.5 g of  $\text{UO}_2$ . The slurry was stirred and the leaching was initiated by adding the required amount of sodium hypochlorite. In each test, a blank set (without sodium hypochlorite) was carried out to take care of aerated oxidation of  $\text{UO}_2$  as all experiments were carried out in the presence of air. The blank value for a given time was subtracted from the sample value. All solution pH measurements were conducted with a combined pH electrode and all the values are between 8.5 and 8.7. The progress of the leaching reaction was followed by withdrawing 1 ml samples at predetermined time intervals and analyzing for dissolved uranium by the spectrophotometric method<sup>15</sup>.

The rate of uranium extraction (R) expressed in terms of fraction of  $\text{UO}_2$  dissolved per minute was calculated for each set of leaching tests after 30 min of treatment from the slopes of fraction reacted ( $\alpha$ ) vs. time plots. Only the linear sections of the graphs were taken for kinetic analysis.

The order of reaction with respect to sodium hypochlorite concentration was derived from the plot of  $\lg k$  vs.  $\lg [\text{OCl}^-]$ <sup>16</sup>.

The apparent activation energy  $E_a$ , was calculated by differential approach<sup>17</sup> by slope of the  $\lg t_\alpha$  vs.  $1/T$ . A method of linear regression analysis was employed in the determination of kinetic parameters<sup>18</sup>.

## RESULTS AND DISCUSSION

### Effect of stirring speed

The effect of stirring speed was investigated using a turbine type impeller with a diameter about a quarter of the reactor diameter. A minimum stirring speed of

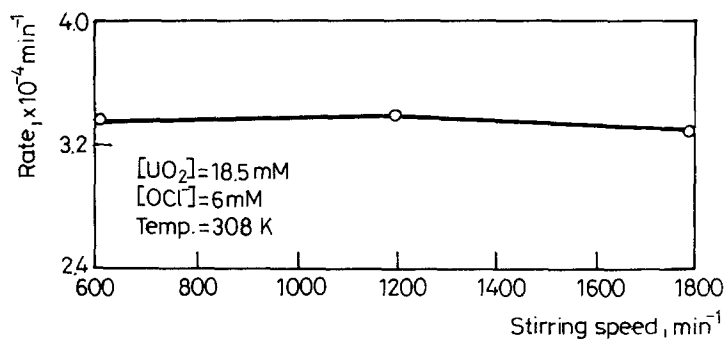


Fig. 1. Effect of stirring speed on the rate of uranium dioxide dissolution

$600 \text{ min}^{-1}$  was found necessary to keep all the  $\text{UO}_2$  particles in suspension. Further increase in stirring speed did not influence the rate of dissolution as shown in Fig. 1. From this result it can be said that the dissolution process is possibly not diffusion-controlled.

#### Effect of temperature

The effect of temperature (303 to 318 K) on the fraction of  $\text{UO}_2$  dissolved at a fixed initial hypochlorite concentration of 6 mM and stirring speed of  $900 \text{ min}^{-1}$  is shown in Fig. 2. It can be seen that  $\alpha$  vs.  $t$  plots become increasingly nonlinear as the temperature increases. Since the integrated rate expression was not known at this stage, a differential approach was made to determine the activation energy. Accordingly, a plot of  $\ln t_\alpha$  against  $1/T$  at  $\alpha = 0.05, 0.1$  and  $0.15$  was obtained (Fig. 3) and an activation energy value of the order of  $57 \text{ kJ mol}^{-1}$  was found. Such a relatively high activation energy coupled with the earlier finding that the rate of leaching was independent of stirring speed indicates a chemical reaction-controlled behavior for the dissolution of  $\text{UO}_2$  in carbonate-bicarbonate media.

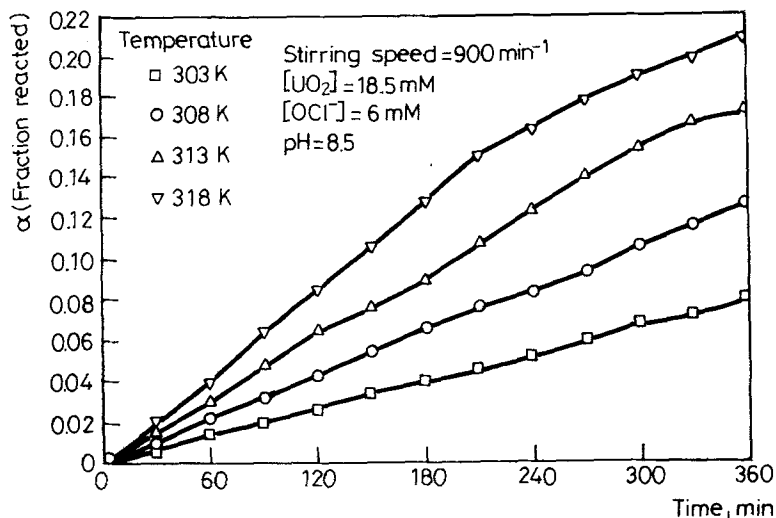


Fig. 2. Effect of temperature on the dissolution of uranium dioxide powder

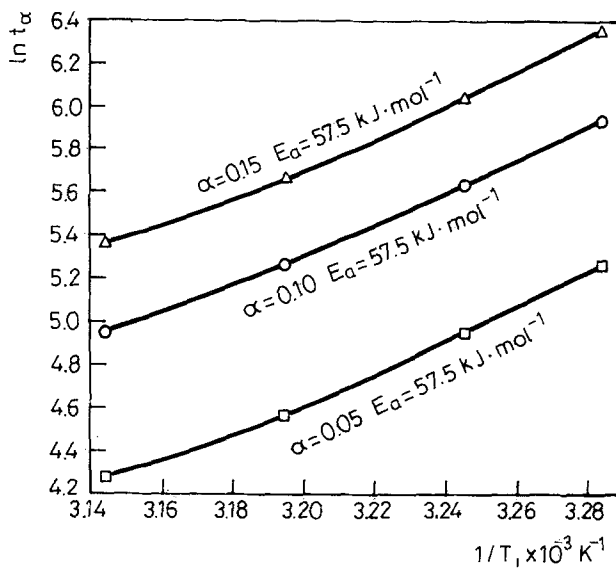


Fig. 3. Activation energy plots by differential approach

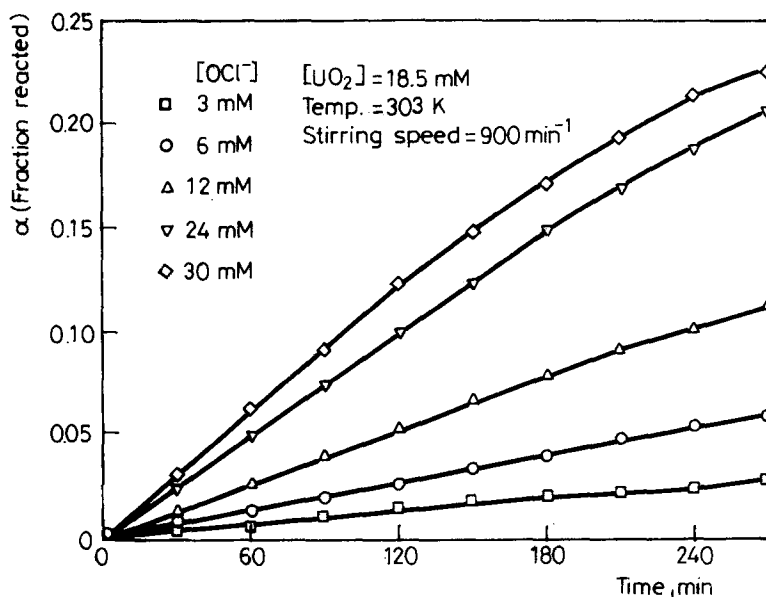


Fig. 4. Effect of hypochlorite concentration on the dissolution of uranium dioxide powder

#### Effect of sodium hypochlorite concentration

A series of leaching experiments were conducted at 303 K,  $900 \text{ min}^{-1}$  and  $\text{UO}_2$  concentration of 18.5 mM, with varying hypochlorite concentration (Fig. 4). The rate of dissolution increases with increasing NaOCl concentration and reaches an optimum value at 0.175M, which corresponds to 70% dissolution at 180 min of treatment. Above the optimum NaOCl concentration, the rate remains constant and does not increase with further increase in hypochlorite concentration (Fig. 5). At higher hypochlorite concentration the increased hydroxide content probably causes a precipitation of the dissolved uranium as sodium uranate. The slope of the plot of  $\lg R$  vs.  $\lg [\text{OCl}^-]$  (Fig. 6) indicates the order of reaction with



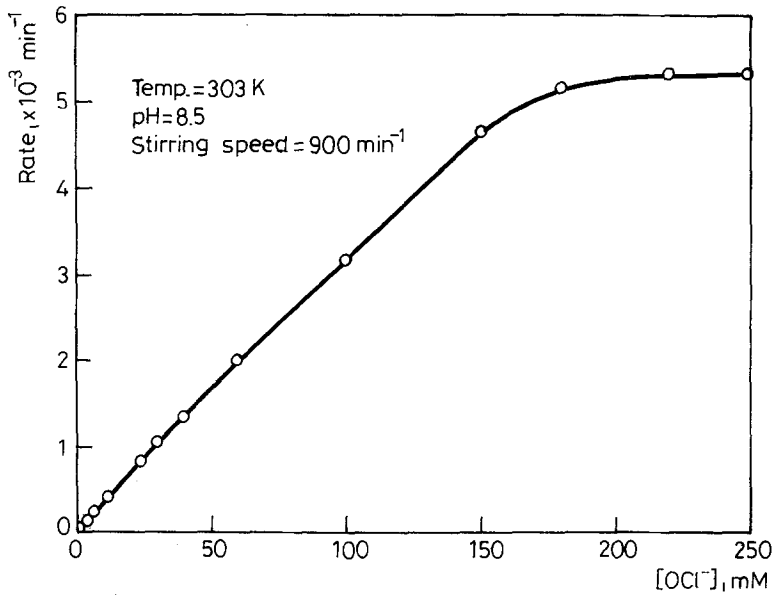


Fig. 5. Effect of sodium hypochlorite concentration on the rate of  $\text{UO}_2$  dissolution

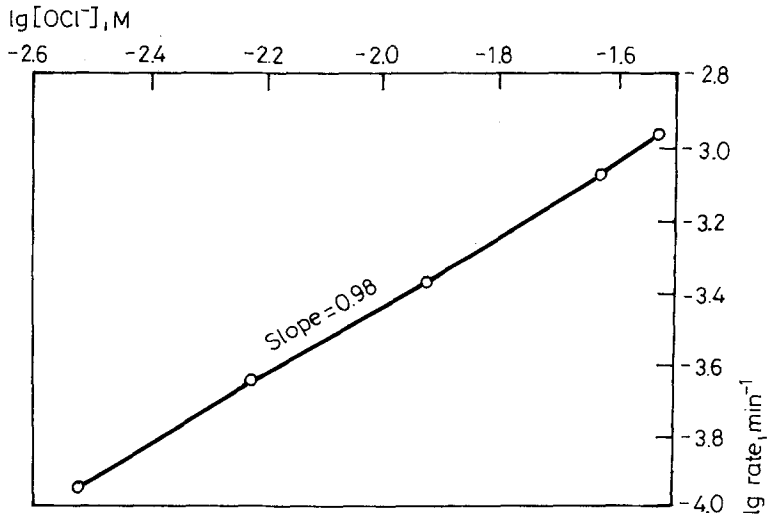
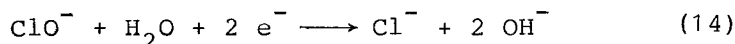
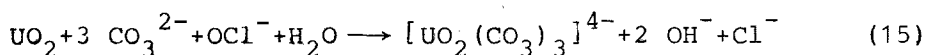


Fig. 6. Determination of the order of reaction with respect to sodium hypochlorite concentration

respect to sodium hypochlorite concentration, which was found to be approximately equal to one. Estimation of chloride ions were done, and found to be increasing with increasing hypochlorite concentration; the reduction of sodium hypochlorite can be written as



The overall reaction by using Eq. (9) is given as



#### CONCLUSIONS

- Leaching of UO<sub>2</sub> in alkaline medium with sodium hypochlorite as an oxidant was found to be slow.
- The dissolution of UO<sub>2</sub> was found to be independent of the stirring speed.
- The order of reaction with respect to sodium hypochlorite concentration was found to be unity.
- The dissolution rates were found to be chemically controlled possibly by the chemical reaction occurring at the UO<sub>2</sub> surface.

The data presented in this study are preliminary in nature and additional work is still needed in order to apply the results of this experiment for uranium ores.

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