RECOVERY OF URANIUM FROM URANIUM RESIDUE BY ALKALINE LEACHING

By

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ABSTRACT

The purpose of this work was to recover uranium from residue originating from the production of molybdenum -99. Carbonate solutions containing hydrogen peroxide or oxygen gas as oxidants were used as leachants. Experimental parameters included: different peroxide and carbonate concentrations, dissolution time and temperature.

Results indicate complete dissolution of the residue at 60 ^{o}C, after thirty minutes, in ammonium carbonate solution enriched with hydrogen peroxide. Almost two hours were needed to achieve the same extent in the presence of oxygen. The yield and rate of uranium extraction were found to increase as a function of both temperature, in the range of 25-60 ^{o}C, and hydrogen peroxide concentration.

The leaching kinetics were determined for various leaching conditions and the activation energy was found to be 45.5kJ/mol. The order of reaction with respect to uranium concentration was found to be unity.

Keywords: uranium, residue, molybdenum production process, alkaline leaching, leachants, oxidants, rate, activation energy.

1. INTRODUCTION

Due to the degree of enrichment of uranium that is found in the uranium residue originating from the production of molybdenum -99, the South African Nuclear Energy Corporation (Necsa) intends to dissolve the residue and recover the uranium content.

Currently this corporation has on hand a backlog of uranium residue that has been stored for many years. Reprocessing of the residue will enable recycling of a precious commodity that can be used to manufacture molybdenum target plates for the production of medical isotopes.

Although this dissolution can be done using acidic solution, it was thought that ammonium carbonate together with hydrogen peroxide could be applied to the residue. Besides this, the use of alkaline solution means that the environment in which the process takes place is non-corrosive and therefore does not pose any hazard to the hot cell. Also, the alkaline dissolution using carbonate is highly selective for uranium and results in the formation of the soluble uranyl tri-carbonate complex (Merritt, 1971).

Early work carried out at Necsa on simulated material, involved the use of various dissolution mediums such as, sodium carbonate/bicarbonate mixture with hydrogen peroxide as an oxidant as well as acidic solutions including nitric acid and sulphuric acid (Naidoo, 2005). The degree of dissolution of the uranium in the carbonate/bicarbonate method varied between 60 and 95%. With regard to the acidic medium, the corrosiveness of the solution proved problematic for the hot cell environment in which the process would eventually be implemented. Even though dissolution of the residue could be achieved in both media, the inconsistent dissolution yields and lack of suitability to the processing environment resulted in abandonment of further research into these dissolution processes.

A few years ago, Necsa relaunched a programme that focused on the development of a process to recover and purify the valuable uranium contained in the process residue. This would be advantageous from both a waste and financial perspective. Several technologies were considered being suitable for this application. However, the carbonate based dissolution process offers significant advantages such as the basicity of the process medium which is likely to result in minimal damage to the process equipment. More importantly the insolubility of most of the contaminants present in the uranium residue in the carbonate medium affords a good initial purification which is achieved simultaneously with the dissolution step. Therefore, the goal of this study was to develop an ammonium carbonate based dissolution process using hydrogen peroxide as an oxidant in order to recover uranium contained in the residue. A specific objective of the project is to provide the fundamental kinetics information of the residue dissolution in alkaline media for use in predicting the leaching behaviours and rates of residues arising from molybdenum process.

The uranium content in the residue was believed to be in different oxidation states, predominantly in a U(IV) oxidation state. Thus, knowledge of the data of dissolution of the simpler pure uranium dioxide in carbonate solutions is essential for the reprocessing of the more complex residue. Appropriate conditions such as solid-liquid ratio, type of oxidants and carbonate concentrations were applied to determine the rate laws governing the dissolution. The resulting kinetics model was then used for the dissolution of the residue from the molybdenum process for uranium recovery.

This work has been divided in four main parts:

- The first part concerns the theoretical background of uranium resources and its dissolution in alkaline media. A brief review of the theories on kinetics of reaction and the available literature on dissolution kinetics of uranium dioxide followed by the experimental approach are presented in this part.

- The second part concerns the presentation and discussion of the results obtained during the kinetics study of uranium dioxide dissolution and simulated residue dissolution in alkaline media, respectively.

- The third part concerns the uranium recovery studies by steam striping as well as the interpretation of the results obtained.
- The fourth part concerns the conclusion and recommendations related to the investigations that have been done in the present study.

2. LITERATURE SURVEY

2.1 Uranium resources, minerals, yellow cake

Uranium occurs in hundreds of minerals, the best known being pitchblende, uraninite, and autunite. It also occurs in many phosphate deposits and monazite sand in which it is associated with rare earth elements (Hardy, 2008).

Pitchblende (U_3O_8) and uraninite (UO_2) (see Figure 2.1) are the most common minerals from which uranium is extracted. These minerals are solids with low solubility in water and are mainly found as hydrothermal vein deposits in igneous and metamorphic rock (Kinnaird and Nex, 2008).

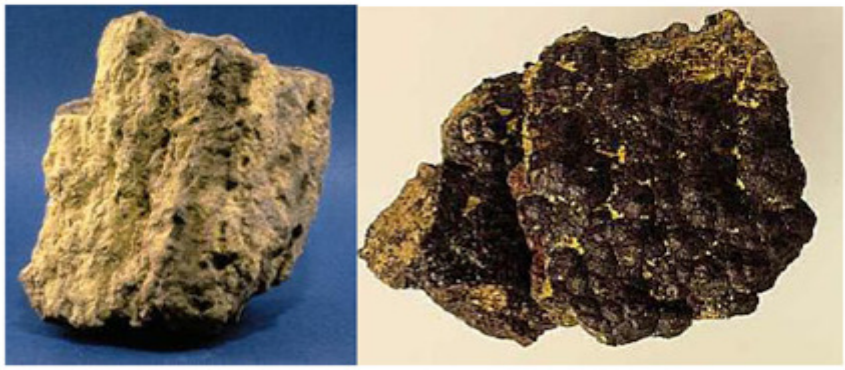


Figure 2-1: Pitchblende (left) and uraninite (right)

Mined uranium ores normally are processed by grinding the ore materials to a uniform particle size and then treating the ore to extract the uranium by chemical leaching.

The leaching process commonly yields dry powder-form material consisting of natural uranium, “yellow cake’ or uranium ore concentrate, which is sold on the uranium market as uranium trioxide.

Yellow cake is a uranium concentrate powder obtained from leach solutions, in the intermediate step in the processing of uranium ores. The name yellow comes from the color and texture of the concentrates produced by early mining operations (www.wikipedia.com).

2.2 Uranium-molybdenum residue

The residue consists of insoluble precipitate that forms during the dissolution of molybdenum-99 target plates for use in technetium generators. This process was developed by the Karlsruhe Nuclear Research Center in Germany.

During this process, an alloy of enriched uranium and aluminum is irradiated in a thermal neutron flux. After short cooling periods, the plates are dissolved in a strong base medium of sodium hydroxide. This result in the dissolution of the aluminum matrix as well as the fission products: molybdenum, cesium, strontium, barium, antimony, tellurium, iodine and a portion of the ruthenium and zirconium. The insoluble residue that remains contains more than 90% of uranium that is present in a mixture of oxidation states (see Figure 2.2 for an example of simulated residue) (Naidoo *et al*., 2005).

Figure 2-2: Simulated residues containing uranium precipitates.

The residue has not been fully characterized and as a result the oxidation state of the uranium is for the most part unknown. Partial characterization has indicated that the uranium is present as mixed hydrated oxides in either a +4 or +6 oxidation state. Uranium in a +4

oxidation state is believed to be the major component in the residue. An overview on the alkaline leaching of uranium dioxide will hence be presented in the following section.

2.3 Alkaline leaching of uranium dioxide

Where the quadrivalent compound is present, an oxidant is added to convert the uranium to the hexavalent state (Pinkney *et al*., 1962).

Thus, as shown on the Pourbaix diagram (Figure 2.3) for carbonate, oxidative conditions are required for the dissolution of uraninite, and that oxygen is a sufficiently strong oxidizing agent.

Separate investigations done by Schortmann (1958) and Pearson (1958) have demonstrated that the oxidation of uranium from the tetravalent to the hexavalent form proceeds in accordance with three principal steps. Gaseous oxygen is first dissolved into solution and is then adsorbed onto active sites on the uranium dioxide surface. Both of these reactions are relatively fast. The slow and, therefore, the rate determining reaction for the oxidation stage is the rearrangement of the absorbed oxygen on the uranium dioxide, with accompanying oxidation to uranium trioxide.

Torrero and coworkers (1998) have confirmed that the initial oxidation of the surface has to take place first:

Step I: Oxidation of the solid surface:

$$UO_2 + O_2 = UO_3 \qquad [1]$$

They suggested that after the initial oxidation of the surface, two parallel processes may occur: Step 2, favoured at acidic pH, which implies the coordination of one proton to the surface and the subsequent fast dissolution of the surface complex. Step 3, favoured at pH above 12, where the hydroxyl groups of water attach to the surface of uranium trioxide to form an insoluble compound:

Step II: Surface coordination of H^+:

$$UO_3 + H^+ = UO_2(OH)^+ (aq) \qquad [2]$$

Step III: Surface coordination of H_2O

$$UO_3 + H_2O = UO_2(OH)_2 \quad [3]$$

Thus, uranium dioxide is expected to dissolve under oxidizing conditions; the solubility increasing drastically on oxidation from uranium (IV) to uranium (VI). After oxidation, the second step in uranium dioxide dissolution is the formation and stabilization of the uranyl ions in solution.

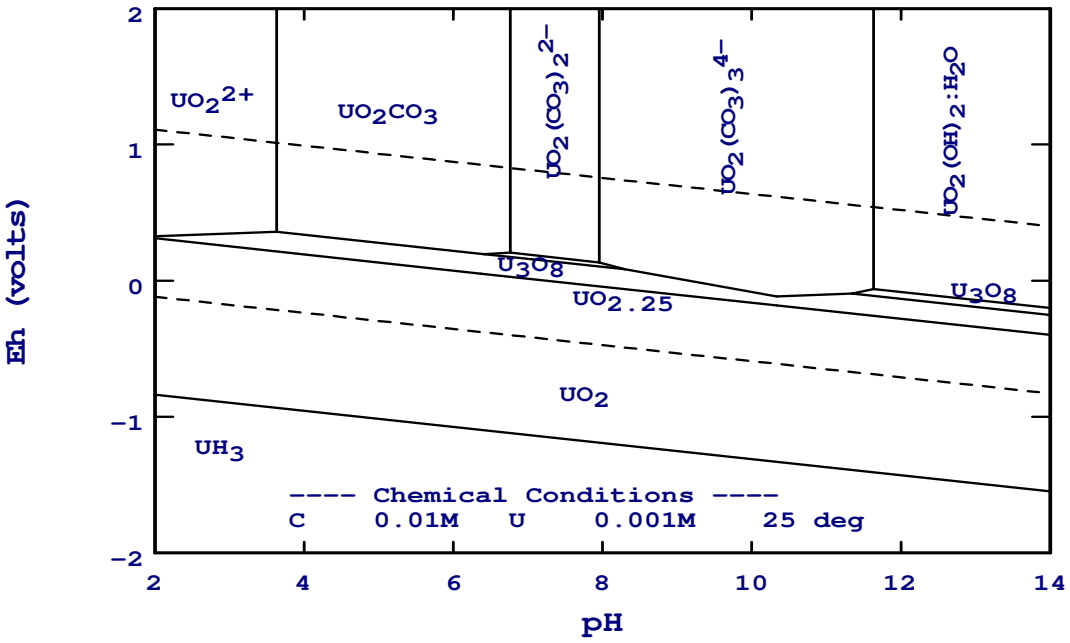


Figure 2-3: Uranium Pourbaix Diagram (Software: Stabcal W32)

As indicated in Figure 2.3 above, under oxidizing conditions, dissolved uranium is predicted to exist as the cation, uranyl (UO_2^{2+}), up to a pH 4, and as neutral or anionic carbonate species for pH values above 4. Uranium will precipitate above pH 11.

Although uranyl ions can form stable, soluble complexes in acidic solutions, the use of a carbonate solution remains more advantageous: the alkaline dissolution is highly selective and results in the formation of the soluble uranyl tri-carbonate complex. Besides this, the alkaline environment is non-corrosive and therefore will not pose any hazard to the hot cell.

It has also the advantage of allowing a pure uranium product to be precipitated directly from the leach liquor.

Carbonate solutions do not exhibit leaching activity for U (IV) compounds in the absence of oxidants. Therefore oxidants are needed for an effective dissolution of uranium dioxide in carbonate solution. More researchers give preference to hydrogen peroxide to convert uranium (IV) into uranium (VI). The choice of the latter reagent is substantiated by its high oxidative power in carbonate media and the ability of the peroxide group to function as a ligand to form carbonate peroxide uranyl complexes, thus increasing solubility of uranium (VI) in carbonate solutions (Stepanov *et al*., 2011).

The main reactions in alkaline leaching of uranium dioxide are represented by the following equations (Pinkney *et al*., 1962).

Oxidation to hexavalent state

$$2UO_2 + O_2 = 2UO_3 \quad [4]$$

Dissolution by carbonate

$$UO_3 + H_2O + 3Na_2CO_3 = Na_4UO_2(CO_3)_3 + 2NaOH \quad [5]$$

Reprecipitation can occur in the absence of bicarbonate

$$Na_4UO_2(CO_3)_3 + 4\ NaOH = Na_2UO_4 + 3\ Na_2CO_3 + 2H_2O \quad [6]$$

Neutralization of hydroxide is achieved by adding bicarbonate into the leach solution and this will prevent the reprecipitation of part of the dissolved uranium through reaction with hydroxyl ion.

$$NaOH + NaHCO_3 = Na_2CO_3 + H_2O \quad [7]$$

Overall reactions 5, 6 and 7 can be represented as

$$UO_3 + Na_2CO_3 + 2NaHCO_3 = Na_4UO_2(CO_3)_3 + H_2O \quad [8]$$

A variation of alkaline leaching is the use of ammonium carbonate instead of sodium carbonate. The main advantages due to the replacement of sodium ion by ammonium ion are:

- No bicarbonate is required to remove the hydroxide formed in the reaction because the solution is naturally buffered at pH 9. This is due to the ammonia-ammonium buffer which buffers in this pH region.

- Precipitation may be carried out by simply heating the solution: sodium hydroxide is not required for precipitation; the solution is simply boiled and swept with steam or air to remove carbon dioxide and ammonia.

- Reagents are easily recovered for re-use

The equations below represent the main reactions taking place:

$$3\ (NH_4)_2CO_3 + UO_2 + ½O_2 + H_2O = (NH_4)_4UO_2(CO_3)_3 + 2NH_4OH \quad [9]$$

$$NH_4OH + NH_4HCO_3 = (NH_4)_2CO_3 + H_2O \quad [10]$$

$$\text{Precipitation: } (NH_4)_4UO_2(CO_3)_3 + \text{heat} = 4NH_3 + 3CO_2 + UO_3 \,.\, 2H_2O \quad [11]$$

$$\text{And regeneration: } 2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3 \quad [12]$$

When the uranium dioxide is oxidatively dissolved in a carbonate solution containing hydrogen peroxide, uranium oxidizes and forms a series of carbonate-peroxide complexes, which ultimately convert to the soluble uranyl carbonate anion ($UO_2(CO_3)_3^{4-}$). The overall dissolution stoichiometry for uranium dioxide is as follows:

$$UO_2 + H_2O_2 + 3(NH_4)_2CO_3 = (NH_4)_4UO_2(CO_3)_3 + 2NH_4OH \quad [13]$$

Actual consumption of hydrogen peroxide was found to be greater than predicted by reaction 13 because of the formation and decomposition of various uranyl peroxide-carbonate complexes.

$$UO_2(CO_3)_3^{4-} + H_2O_2 = UO_2(CO_3)_2(O_2)^{4-} + 2H^+ + CO_3^{2-} \quad [14]$$

The formation of these mixed uranyl peroxide-complexes has been found to release hydrogen ions (eq 14). But as these mixed complexes decompose, with lifetimes from hours to weeks, to oxygen, water and carbonate complexes, these hydrogen ions will be consumed (Chuck *et al.*, 2011)

$$2O_2^{2-} + 4H^+ = 2H_2O_2 = 2H_2O + O_2 \quad [15]$$

The formation of uranyl peroxide-carbonate complexes ions has been confirmed by Dong (2010) while dissolving uranium from SIMFUEL using sodium carbonate and hydrogen peroxide solutions. This proves that in alkaline leaching, hydrogen peroxide plays two combined roles described by Peper *et al*., (2004): it acts as an oxidant that greatly accelerates the rate of dissolution and also acts to complex with uranium to form mixed peroxide-carbonate complex.

It can be seen from the review of alkaline leaching of uranium dioxide presented that the presence of carbonate affects the kinetics for uranium dioxide oxidation since it forms soluble complexes with the oxidation product, uranyl ion, and thereby maintains a larger surface area accessible to oxidation.

Furthermore, when considering the choice of an oxidant for the oxidation process of uranium dioxide, the use of hydrogen peroxide presents more advantages than that presented by the use of oxygen gas.

However, factors such as reagents concentration, temperature, and agitation speed and particle size have to be taken into account due to their influence on the dissolution rate of uranium dioxide. Therefore, the kinetics study remains an important step during the dissolution process of uranium dioxide in alkaline media.

In order to have a better understanding of the dissolution kinetics of uranium dioxide, a background review to kinetics of reaction is presented in the next section. This is followed by a review of some studies that have been conducted on the dissolution kinetics of uranium dioxide in carbonate media.

2.4 Background to kinetics of reaction

2.4.1 Fundamentals

Chemical kinetics deals with the experimental determination of reactions rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero order reactions (for which reaction rates are independent of concentration), first order reactions, and second order reactions, and can be derived for others.

Under kinetic control, chemical reaction rates are markedly influenced by temperature. They are also influenced by physical state of a reactant, catalysts and concentration. The effect of temperature was noted early in scientific development and it was in 1889 that Arrhenius explained the simple exponential form.

Arrhenius argued that in order for reactants to be transformed into products, they first needed to acquire a minimum amount of energy, called the activation energy Ea. This energy must be overcome in order for a chemical reaction to occur.

It is generally true that increasing the activation energy of a given reaction slows it down and lowering it speeds it up. When the activation energy is high, reactions often proceed too slowly to be useful. It can be seen that either increasing the temperature or decreasing the activation energy will result in an increase in rate of reaction (AICHEMI, 1981).

The rate constant can be presented as:

$$K = zpe^{-Ea/RT} \qquad [16]$$

Where z is the collision frequency, p is called the steric factor and reflects the fraction of collisions with effective orientations, and $e^{-Ea/RT}$ represents the fraction of collisions with sufficient energy to produce a reaction. This expression is most often written in the form:

$$K = Ae^{-Ea/RT} \qquad [17]$$

This is called the Arrhenius equation. In this equation, T represents temperature in degrees Kelvin and R is the universal gas constant. *A* replaces *zp* and is called the frequency factor for the reaction. Ea is the activation energy.

The reaction may be chemical, diffusion controlled or under mixed control. Table 2.1 lists the differences between chemical and diffusion controlled reactions.

Table 2.1: Characteristics of a chemical and diffusion controlled reaction

Chemical controlled reaction	**Diffusion controlled reaction**
No dependence of reaction rate on agitation; only necessary to keep particles in suspension	Highly dependent on reagent concentration, agitation speed and interfacial area (particle size)
Reaction rate highly temperature dependent	Effect of temperature is very small
Activation energy is ≥ 40 kJ/mol	Activation energy is below 20 kJ/mol

The reaction is under mixed control when the value of the activation energy is between 20 kJ/mol and 40 kJ/mol.

Zero-order reactions

A zero order reaction is one that occurs at constant rate. This rate is independent of the concentration of the reactants. A reaction is zero order if concentration data are plotted versus time and the result is a straight line (Levenspiel, 1999). The slope of this resulting line is the negative of the zero order rate constant k.

For the reaction: aA + bB = Rr + sS the integrated rate law for zero-order with respect to A is written as:

$$-[A]_t = k.t + [A]_0 \qquad [18]$$

First-order reactions

A first order reaction is one whose rate depends on the concentration of a single reactant raised to the first power (Levenspiel, 1999) or whose reactants exponents, when summed, equal one. Relating, for example, the initial concentration of $[A]_o$, to its concentration at any other time t, $[A]_t$:

The integrated first rate law is:

$$\ln[A]_t = -k.t + \ln[A]_o \qquad [19]$$

This equation has the form of the general equation for a straight line, $y = mx + b$, in which m is the slope and b is the y-intercept of the line. Thus, for a first order reaction, a graph of $\ln[A]_t$ versus time gives a straight line with a slope of $-k$ and y-intercept of $\ln[A]_o$.

Second order reaction

A second order reaction is one whose rate depends on the reactant concentration raised to the second power or on the concentrations of two different reactants, each raised to the first power (Levenspiel, 1999). For a reaction that is second order, the rate law is given by:

$$\frac{d}{dt}\left(\frac{1}{[A]_t}\right) = \frac{d}{dt}\left(\frac{1}{[A]_o}\right) + k \qquad [20]$$

Integrating both sides, this rate law is given by:

$$\frac{1}{[A]_t} = k.t + \frac{1}{[A]_o} \qquad [21]$$

If the reaction is second order, a plot of $1/[A]_t$ versus t will yield a straight line slope equal to k and a y-intercept of $1/[A]_o$.

2.4.2 Dissolution kinetics of uranium dioxide

Some studies on the dissolution kinetics of uranium dioxide particles have been conducted to monitor the influence of reagent concentration, type of oxidants and temperature on the dissolution rate of uranium dioxide in alkaline solution.

Smith *et al*. (2009) reported that the dissolution rate of uranium dioxide powder increases linearly over the temperature range of 15-60 degrees Celsius in 1M ammonium carbonate with 0.1M hydrogen peroxide.

This has been confirmed by Pierce *et al*. (2005) who observed that the rate of uranium dioxide dissolution in carbonate solution increased by an order of magnitude with a 30 degree Celsius increase in temperature.

Investigating the oxidative dissolution of uranium dioxide in alkaline media, Clarens *et al.* (2004) observed that the dissolution rate of uranium dioxide increased with increasing the hydrogen peroxide concentration.

The rate of uranium dioxide dissolution under oxidizing conditions in carbonate/bicarbonate media was found to be directly proportional to the total hydrogen carbonate concentration by Grandstaff (1976). Generally, within the pH range from 8.3 to 10.3 the rate of dissolution of uranium dioxide is independent of carbonate/bicarbonate ratio because the carbonate and bicarbonate ions play equivalent roles, the tri-carbonate species being dominant throughout the range.

Thus, it can be seen that the concentration of the reagents and the temperature of the solution have an impact on the dissolution rate of uranium dioxide in carbonate media. However, the working temperature, while leaching with ammonium carbonate in an open beaker, must be kept below 60 degrees Celsius as its solutions decompose to ammonia and carbon dioxide above this temperature (Robert *et al*., 1981).

The following section will elaborate upon the experimental approach used to achieve the objectives of this study.

2.5 Experimental approach

The experimental approach involved first the dissolution of uranium dioxide samples in an open beaker or in the autoclave. Then, the resultant kinetics model was applied on uranium-molybdenum residue samples for uranium recovery.

Leaching variables considered were temperature, solid-liquid ratio and reagent concentration. Single variable testing was used for the optimization of the dissolution parameters.

In this approach, series of leaching tests were taken while changing only one variable at a time i.e. maintaining the variables at fixed values for a given set of measurement. The next series of tests would then focus on the influence of another variable on the dissolution outcome, all other factors remaining constants (Hayes, 2003).

3. EXPERIMENTAL

3.1 Materials and reagents

On the basis of the reviews and objectives presented in the previous chapters, the materials and methods for this project are presented in this chapter. Supplementary investigations done on uranium recovery from ammonium carbonate solution are also presented.

3.1.1 Uranium dioxide fuel pellets

Fuel pellets of uranium dioxide (99.9 % uranium dioxide) were used as sample. This sample was supplied by Nuclear Energy Corporation of South Africa (Necsa).

The pellets were ground in the mortar prior to the start of the experiments. 70 grams of the sample with a particle size of 38-106µm were immersed for 48 hours in a solution of 1 M ammonium carbonate, prepared with oxygen free water. The aim was to dissolve oxidized phases that may have formed on the surface of the pellets due to oxidation by air.

The sample was then washed with water free of oxygen and leached.

3.1.2 Simulated residue

100 g of simulated residue with a particle size of 38-106µm were used. The material was supplied by Nuclear Energy Corporation of South Africa and was not pre-treated for oxide layers removal prior to leaching. This was due to the fact that the sample was kept in sealed container and was not exposed to atmospheric air.

A sample was sent to Pelindaba Analytical Lab for X-Ray fluorescence analysis in order to determine the major components present in the residue. The results are indicated in Table 3.1.

Table 3.1: Semi-quantitative XRF results from analysis of the simulated residue

Determination	**Results**
Phosphorus	Trace
Silicon	Trace
Sodium	Minor
Uranium	Major
Aluminum	Minor

Another portion of sample was sent for X-ray diffraction in order to determine the actual oxidation state of this residue (see Figure 3.1).

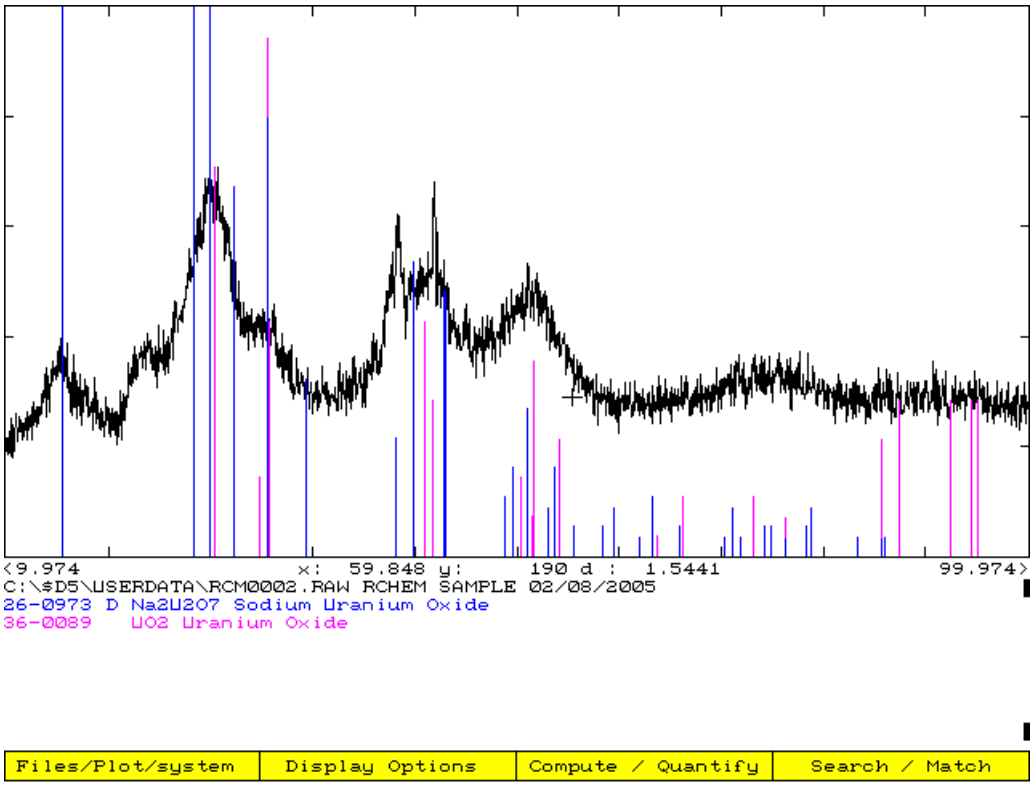


Figure 3-1: The diffractogram of the simulated residue

The diffractogram of the uranium sample (simulated) matched closely to that of uranium dioxide and $Na_2U_2O_7$. These compounds of uranium were expected. The uranium is therefore present in a mixture of oxidation states.

3.2 Experimental techniques

3.2.1 Batch leaching

Tests were performed in an open beaker (50 ml) and the mixture of ammonium carbonate and hydrogen peroxide was then heated using a hot plate with magnetic stirrer and a temperature-controlled thermostat (Heidolph MR 3001 K).

0.5 grams of simulated residue was added into ammonium carbonate solution and hydrogen peroxide of an appropriate concentration. The mixture was then heated to the required temperature with continuous stirring at different time until the end of the experiment.

Solution pH was measured using a Metrohm 704 pH-meter with a combination pH electrode and temperature probe. The meter and electrode were calibrated using pH 7.00 and 10.00 buffer solutions

After dissolution, each solution was allowed to cool to ambient temperature and then filtered through a weighed No 4 Whatman filter paper. The undissolved residue was collected, washed, dried for 24 hours in the oven at 60 ^{o}C and then weighed to determine the amount of the undissolved sample.

Depending on the expected dissolved uranium, solutions collected were analyzed for uranium by use of spectrophotometer technique.

3.2.2 Pressure leaching

The pressure vessel used for the dissolution of the sample was a Parr 4848 reactor controller that was connected to a 4597 Micro Reactor with a 100 ml fixed head (see Figure 3.2). The device has a working pressure up to 207 bars and maximum working temperature of 350 ^{o}C.

0.5 grams of the simulated residue was added into ammonium carbonate and hydrogen peroxide solutions of an appropriate concentration. The mixture was then poured in the vessel, which was sealed, and then heated to the required temperature with continuous stirring (500 rpm) until the end of the experiment. All work with ammonium carbonate solutions above 60 ^{o}C was performed in the autoclave as ammonium carbonate decomposes to ammonia and carbon dioxide above this temperature.

Sampling was not possible with this autoclave; therefore analysis was done after the experiment.

The final solution was filtered with Whatman No 4 filter paper and the residue obtained was washed, dried and weighed to determine the amount of the undissolved uranium.

Figure 3-2: Micro Reactor, Moveable Head and a 4848 Reactor Controller

Reproducibility tests were done to compare findings with the initial results and ensure accuracy and reliability of the leaching process. All the results from reproducibility tests are found in the Appendix 2.

The experimental conditions used for batch and autoclave leaching are shown in Table 3.2 below.

Table 3.2: Experimental conditions used for batch and autoclave leaching

Parameters	**Batch leach**	**Autoclave leach**
Temperature (Degree Celsius)	25; 40; 50	60; 80
Dissolution time (Minutes)	30; 60; 90; 120; 240	30; 60; 180
Solid-liquid ratio	1:40; 1:60; 1:80	1:60; 1:80
Particles size (µm)	38-106	38-106
Agitation speed (rpm)	500	500
$[(NH_4)_2CO_3]$	0.1 M; 0.5 M; 1 M	0.1 M; 0.5 M; 1 M
$[H_2O_2]$	0.1 M; 0.5 M; 1 M	0.1 M; 0.5 M; 1 M
Oxygen pressure		4 Bar
Total carbonate	0.1 M; 0.5 M; 1 M	0.1 M; 0.5 M; 1 M

3.2.3 Uranium recovery studies

A standard generated leach solution was used for uranium precipitation experiments. These solutions were generated from ammonium carbonate and hydrogen peroxide dissolution of U_3O_8.

An appropriate mass of the compound was added into solutions of ammonium carbonate (1M) and hydrogen peroxide (1M). The mixture was then heated to 60 ^oC with continuous stirring. Complete dissolution was obtained after 3 hours leach. The final pH of solution was 9.1.

Procedure

- pH of the solution was measured prior to the precipitation experiments and after the recovery of uranium
- The uranium concentration was determined using a UV- spectrophotometer before and after precipitation tests
- The effects of initial uranium concentration and the seed added in the form of the precipitate were studied and the recovery optimised
- After each precipitation run, the solution was cooled down to room temperature and filtered with Whatman filter paper (150 mm, 2V)
- Then, the precipitate was washed, dried in a oven for 24 hours (60 ^{o}C)
- Particles size analysis was done on the precipitate using a LEICA DM 4000B Microscope
- Each test was repeated for reproducibility reasons.

3.2.4 Analytical techniques

Only leach solutions were analyzed. The uranium concentration in solutions was determined using the standard hydrogen peroxide-carbonate or the Bromo-Padap spectrophotometric analytical method.

The hydrogen peroxide-carbonate spectrophotometric method is suited to higher uranium concentrations in the 20-200 ppm range. It is based on the intense yellow colour product by the $[UO_2(CO_3)_2OOH]^{3-}$ -complex. The wavelength at which measurements were made was 450nm (see method detail in Appendix 5).

The Bromo-Padap spectrophotometric method is suited to lower concentrations in the 0-20 ppm range. It is based on the intense red colour produced by the complexing of uranyl with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Bromo-Padap). Colour development was allowed for 40 minutes and the measurements wavelength was 578 nm (see Appendix 6).

4. RESULTS AND DISCUSSION

4.1 Uranium dioxide leach kinetics

4.1.1 Effect of peroxide concentration on uranium fuel pellets dissolution

Experiments were performed to determine the rate of leaching uranium dioxide in ammonium carbonate solutions at 25, 40, 50, 60 and 80 ^{o}C. It was observed that, in the absence of an oxidant, it was impossible to dissolve uranium dioxide particles in the various solid-liquid ratios used. This observation is consistent with that reported by Smith *et al.* (2009) who could not dissolve uranium dioxide sample in ammonium carbonate solution without an oxidant.

On the basis of this result, variable concentrations of hydrogen peroxide were used for the dissolution of uranium fuel at different temperatures. Figures 4.1; 4.2 and 4.3 illustrate the impact of hydrogen peroxide concentration on the dissolution of 0.5g uranium fuel in 1 M ammonium carbonate solution at 25; 40 and 50 ^{o}C.

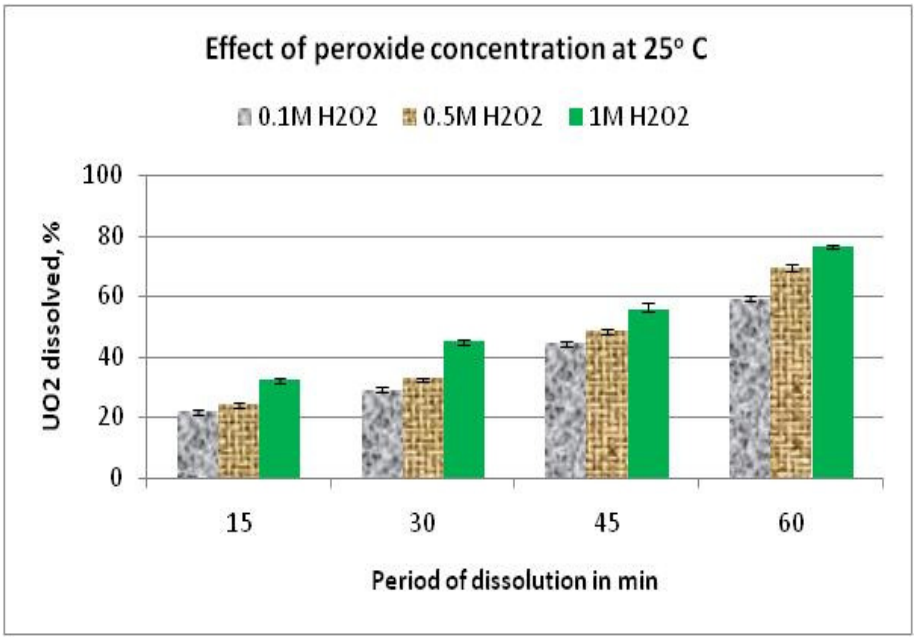


Figure 4-1: Dissolution of 0.5 g uranium dioxide in 1 M ammonium carbonate and variable hydrogen peroxide concentration at 25 ^{o}C. Error bars represent the 3σ error

It can be seen from data shown in Figure 4.1 that the dissolution rate of uranium dioxide increases with the increase of hydrogen peroxide concentration. The rate increases were due to faster oxidation of the U(IV) by hydrogen peroxide and the formation of aqueous uranyl peroxocarbonate species. As seen in Figure 4.1, the dissolution rate increases as the

concentration of hydrogen peroxide increases. Uranium dioxide is completely dissolved within 1 hour at a reaction temperature above 25 °C with hydrogen peroxide at 1 M. See Figure 4.2 and Figure 4.3.

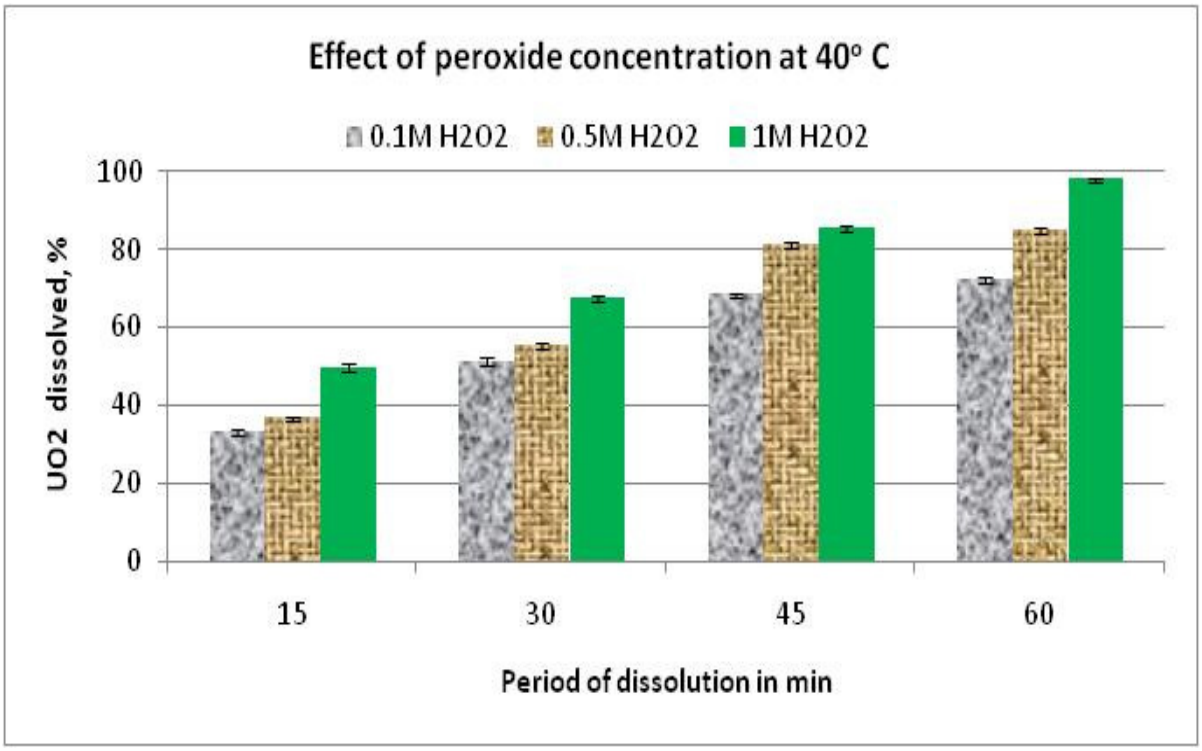


Figure 4-2: Dissolution of 0.5 g of uranium dioxide in 1 M ammonium carbonate and variable hydrogen peroxide at 40 °C. Error bars represent the 3σ error

It is seen, from Figure 4.3 below, that almost 99% of uranium dioxide was dissolved within 1 hour when the temperature was increased from 25 °C to 50 °C and hydrogen peroxide concentration was increased from 0.1 M to 1 M, respectively.

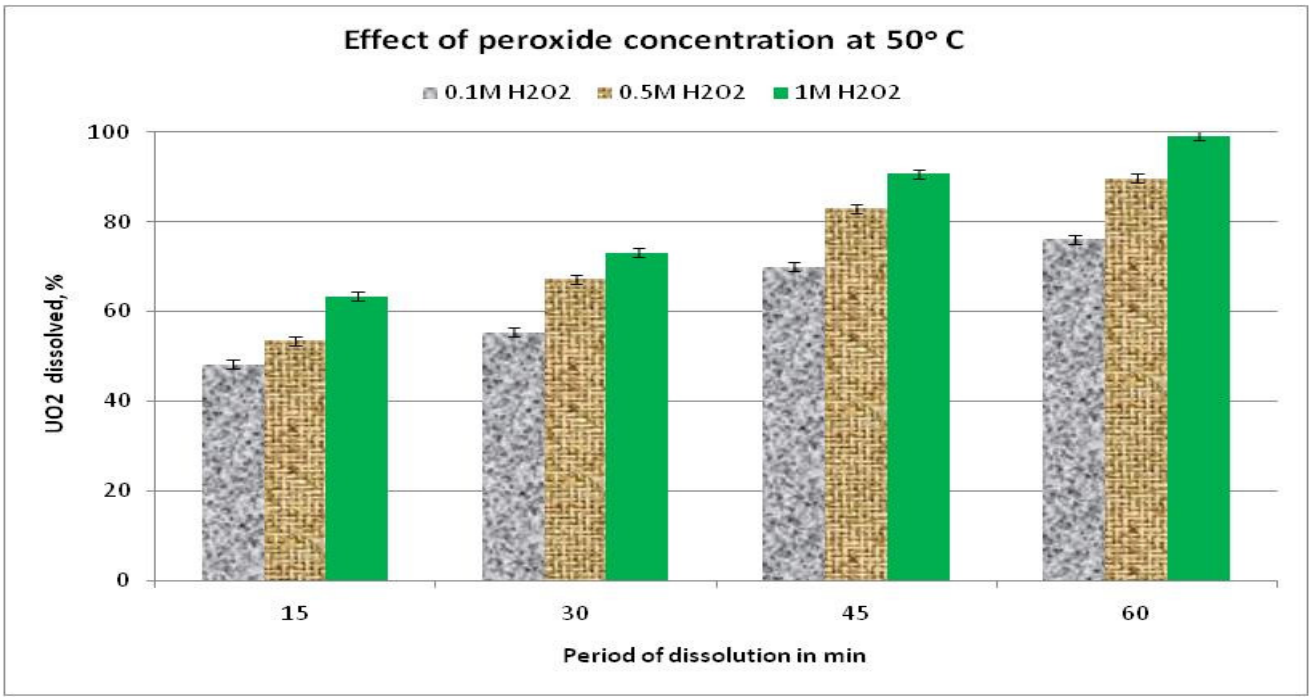


Figure 4-3: Dissolution of 0.5 g of uranium dioxide in 1 M ammonium carbonate and variable hydrogen peroxide at 50 ^{o}C. Error bars represent the 3σ error

The data shown in Figure 4.4 below confirm that the dissolution rate is dependent on the concentration of hydrogen peroxide ranging from 0.1 M to 1 M. An observation that was also made earlier in Section 4.1.1. This observation is consistent to that reported in other work (Smith, 2009; Peper, 2004; de Pablo, 1999). It is therefore important to maintain proper oxidizing conditions during leaching of uranium dioxide in carbonate media to achieve high uranium extraction.

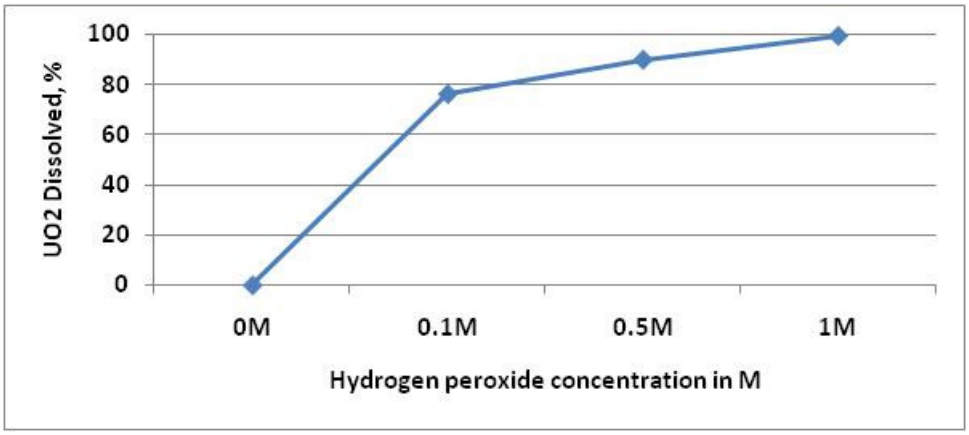


Figure 4-4: Determination of the effect of hydrogen peroxide on the extent of dissolution of uranium dioxide in 1 M ammonium carbonate.

The resultant solutions obtained from uranium dioxide dissolution were red from the first day and became stable yellow within a week. This observation is similar to that reported in the literature and indicates the formation of a uranyl peroxide-carbonate complex, red in colour after dissolution then becoming the stable yellow uranyl-tricarbonate complex ($UO_2(CO_3)_3^{4-}$) within several days (Grenthe *et al.,* 1992).

4.1.2 Effect of temperature on uranium dioxide dissolution

In order to confirm the dependence of dissolution rate of uranium dioxide on temperature, 0.5 g of uranium dioxide was dissolved in 1 M ammonium carbonate and 1 M hydrogen peroxide solutions at various temperatures. The results are shown in Figure 4.5.

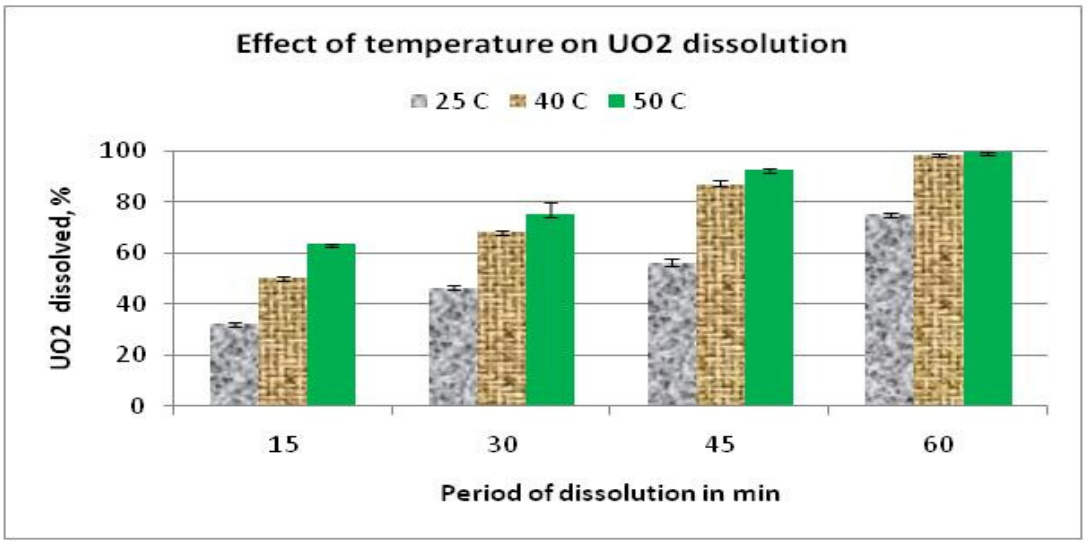


Figure 4-5: Dissolution of 0.5 g uranium dioxide in 1 M ammonium carbonate and 1M hydrogen peroxide at variable temperature. Error bars represent the 3σ error

From the Figure 4.5, it has been shown that the dissolution rate of uranium dioxide increases with temperature within the range of 25-50 ^{o}C, with complete dissolution observed at 40 and 50 ^{o}C after an hour of leaching. It is seen that the leaching reaction is under kinetic control at temperature of 25 ^{o}C and above; similar trend is obtained in spite of the different temperatures used.

These results support those reported by Pablo *et al*. (1999) who observed an increase in the dissolution rate of uranium dioxide in hydrogen carbonate solution by increasing the temperature from 25 to 60 ^{o}C.

As would be expected, the kinetics of leaching improve with increased temperature, but dissolution experiments of uranium dioxide done at elevated temperatures for 1 hour have shown a drop of the dissolution rate from 60 ^{o}C up to 80 ^{o}C (Figure 4.6). This loss of carbonate is due to the decomposition of ammonium carbonate in aqueous solutions at higher temperature. For example, at 80 ^{o}C, Nowak (1989) observed that 1.15 M of ammonium carbonate decomposes to 0.498 M after one hour. This means, in the range of conditions investigated, instead of 4 times excess of carbonate expected in solution, only about 1 time excess is left after decomposition and complexation with uranium. Thus, leaching at 80 ^{o}C appears to be detrimental for uranium dioxide dissolution in ammonium carbonate solution in the range of conditions investigated.

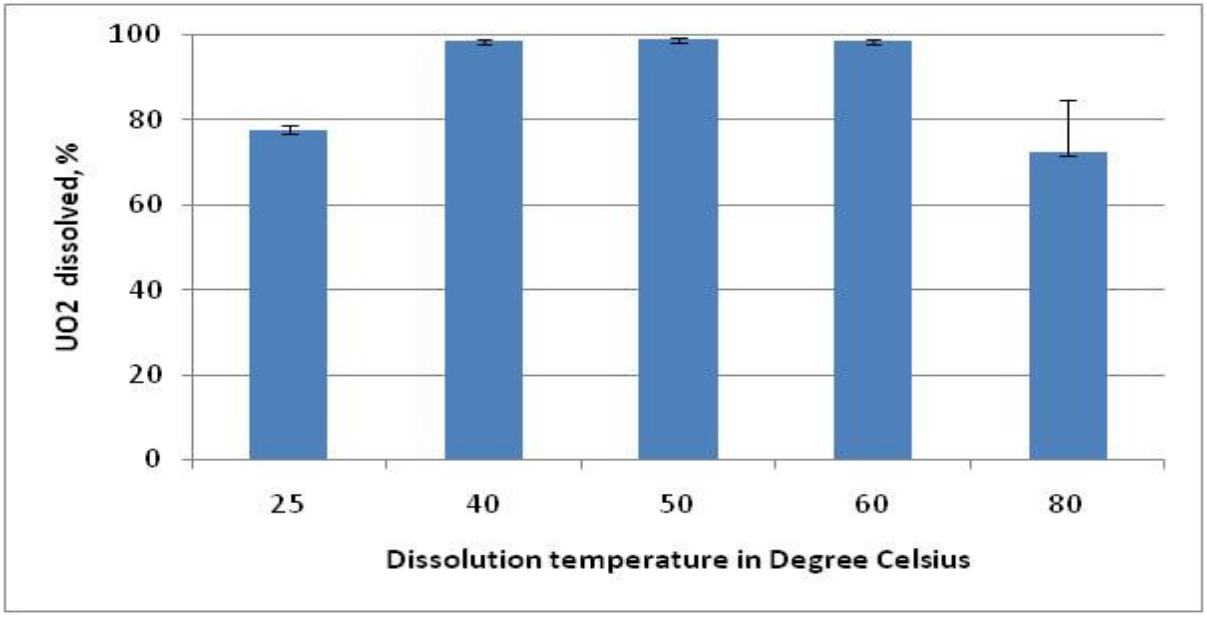


Figure 4-6: Dissolution of 0.5 g uranium dioxide in 1 M ammonium carbonate and 1 M hydrogen peroxide for 1 hour using a pressure vessel. Error bars represent the 3σ error

4.1.3 Effect of solid-liquid ratio on uranium dioxide dissolution

In addition to temperature and hydrogen peroxide concentration, another variable that was suggested to have a substantial impact on the dissolution of uranium dioxide in ammonium carbonate was the solid-liquid ratio (see Figure 4.7).

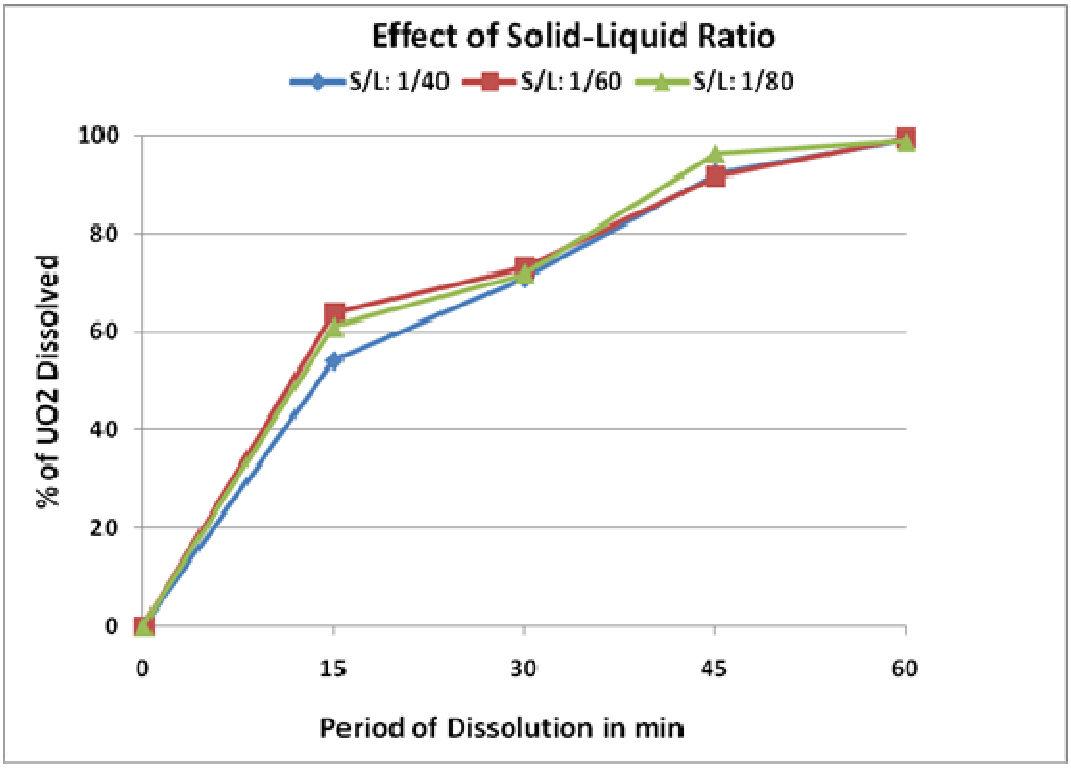


Figure 4-7: Dissolution of 0.5 g uranium dioxide in 1 M ammonium carbonate and 1 M hydrogen peroxide at variable solid-liquid ratio at 50 ^{o}C

The above results indicate that the solid-liquid ratio does not have a remarkable effect on the dissolution rate of uranium dioxide in the range of conditions investigated.

4.1.4 Determining the rate law

The first step in understanding how a given chemical reaction occurs is to determine the form of the rate law. That is, we need to determine experimentally the power to which each reactant concentration must be raised in the rate law.

To decide whether the rate law for uranium dioxide dissolution in ammonium carbonate is first order, second order or zero order, an indication of whether the plot of ln[UO_2] versus time is a straight line or whether the plot of [UO_2] versus time is a straight line has to be found, respectively. The data used to make these plots are found in the Appendix 3.

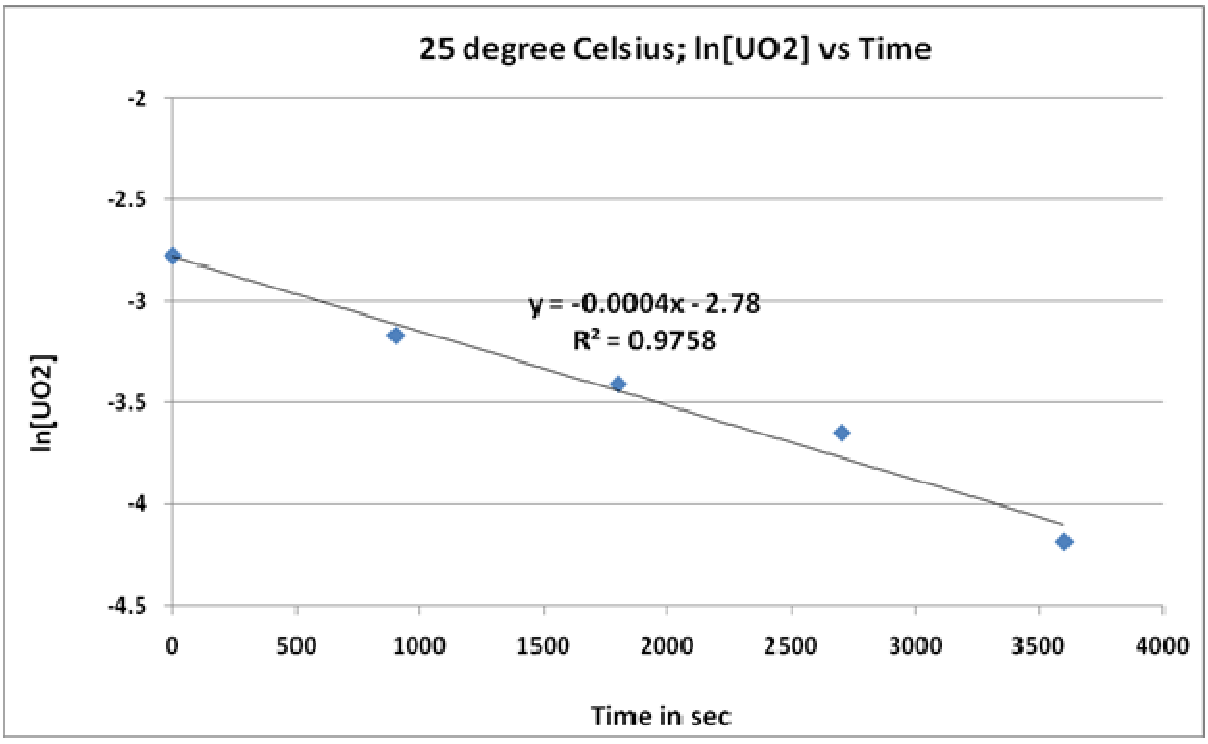


Figure 4-8: First order plot for 25 ^{o}C

It can be seen from the Figure 4.8 above that there is significant relationship between the dissolution time and ln[UO_2].

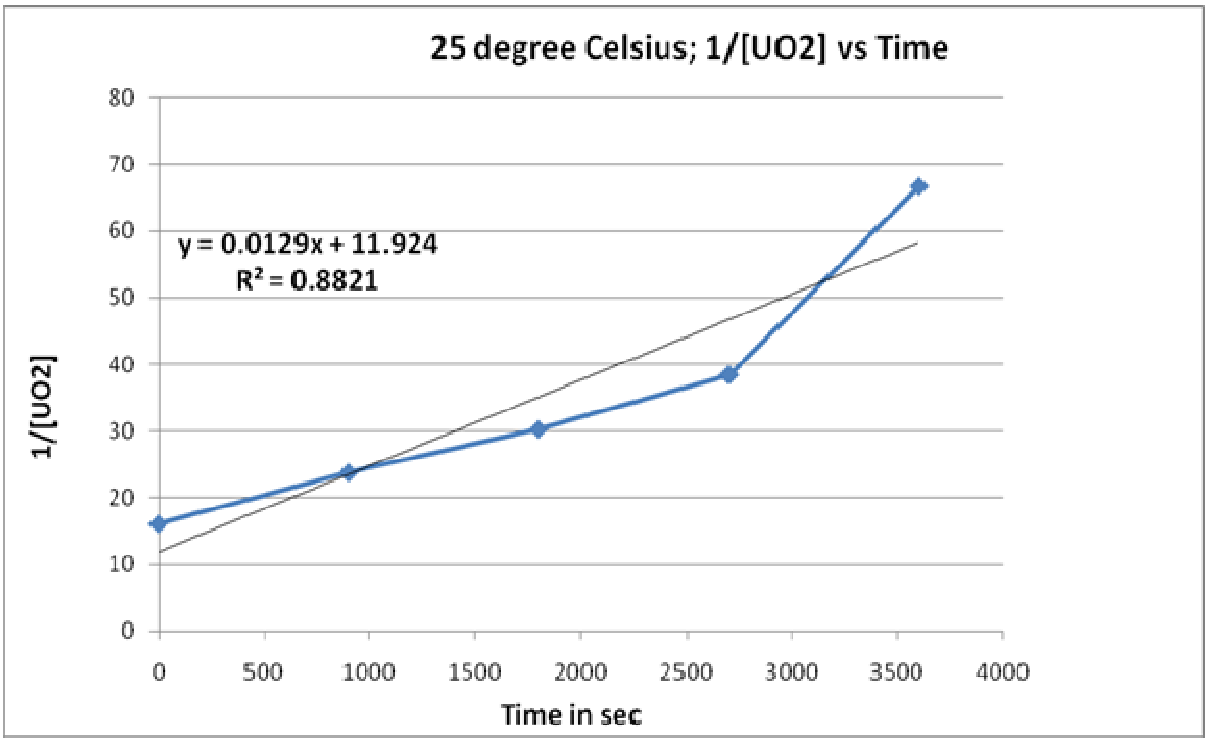


Figure 4-9: Second order plot for 25 ^{o}C

A low R square was obtained in the plot of 1/[UO_2] against time. Almost 88% of the variance is shared between the two variables. This indicates that the data are not well-correlated and there is no significant relationship between the two variables. Thus the rate law for uranium dioxide dissolution is not a reaction of second order under these conditions.

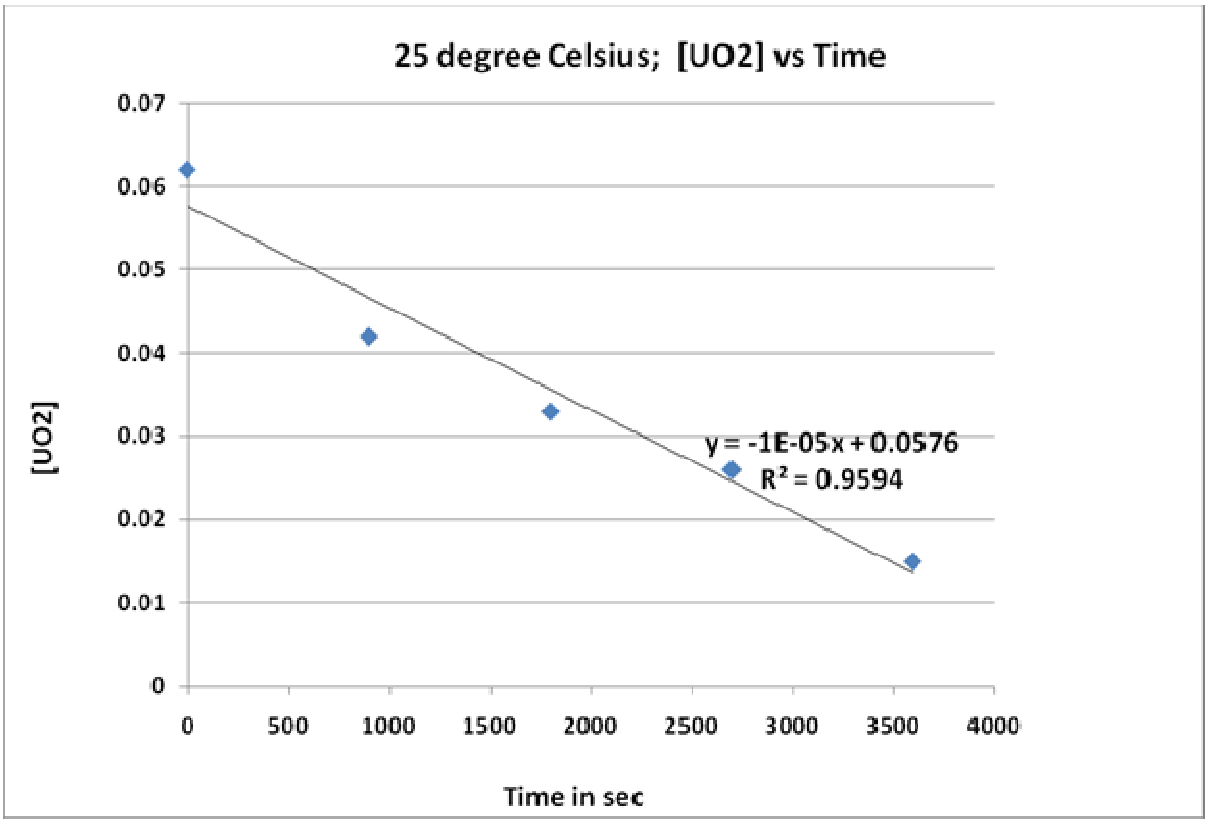


Figure 4-10: Zero order plot for 25 ^{o}C

Compared to the first order plot (see Figure 4.8), the data are not well correlated in the above Figure 4.10 even though the coefficient of determination is higher, the regression line does not fit the data. This confirms that the relationship between the two variables is not certain enough to be useful. Thus, at 25 ^{o}C, the rate law for the dissolution of uranium dioxide in ammonium carbonate solution is not zero order.

Similar observations are found in Figures 4.11 to 4.16 for reaction temperatures of 40 ^{o}C and 50 ^{o}C. Thus the reaction is first order in UO_2 under the reaction conditions used in this work. This observation is consistent with that reported by Sharma *et al.* (1996) who found the order of reaction to be unity while dissolving uranium dioxide in sodium carbonate-bicarbonate solution containing sodium hypochlorite as an oxidant.

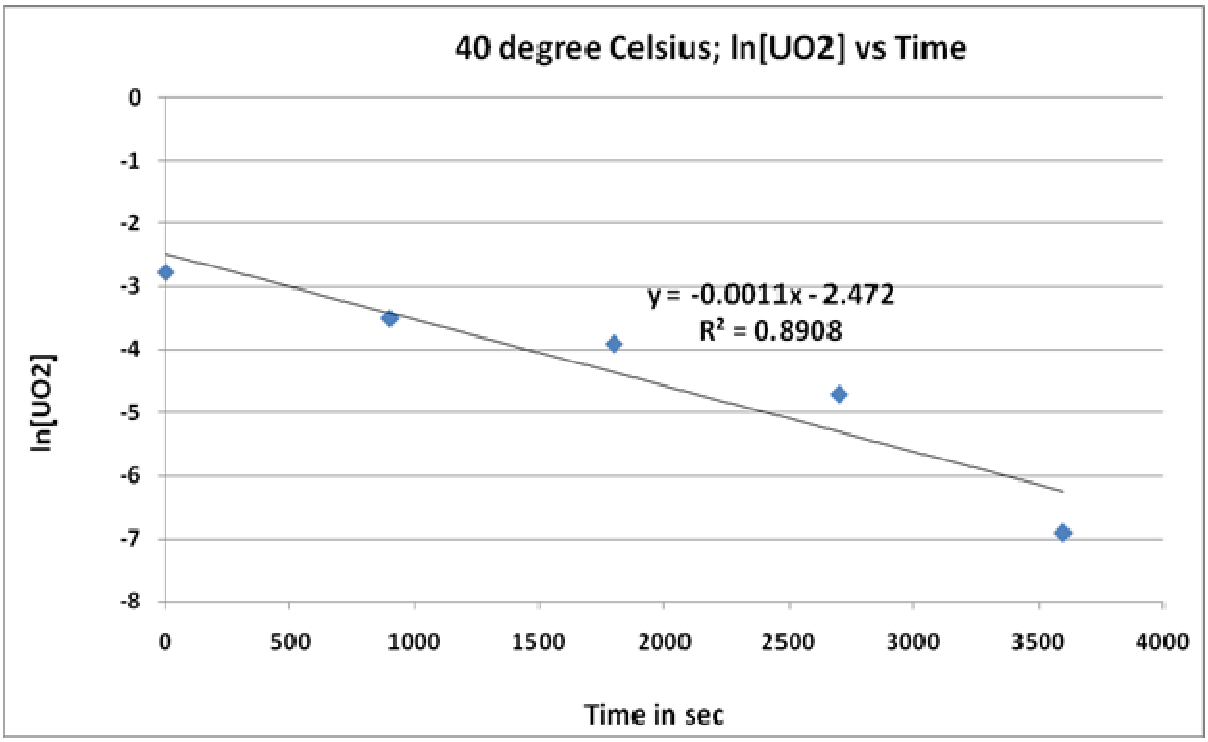


Figure 4-11: First order plot for 40 °C

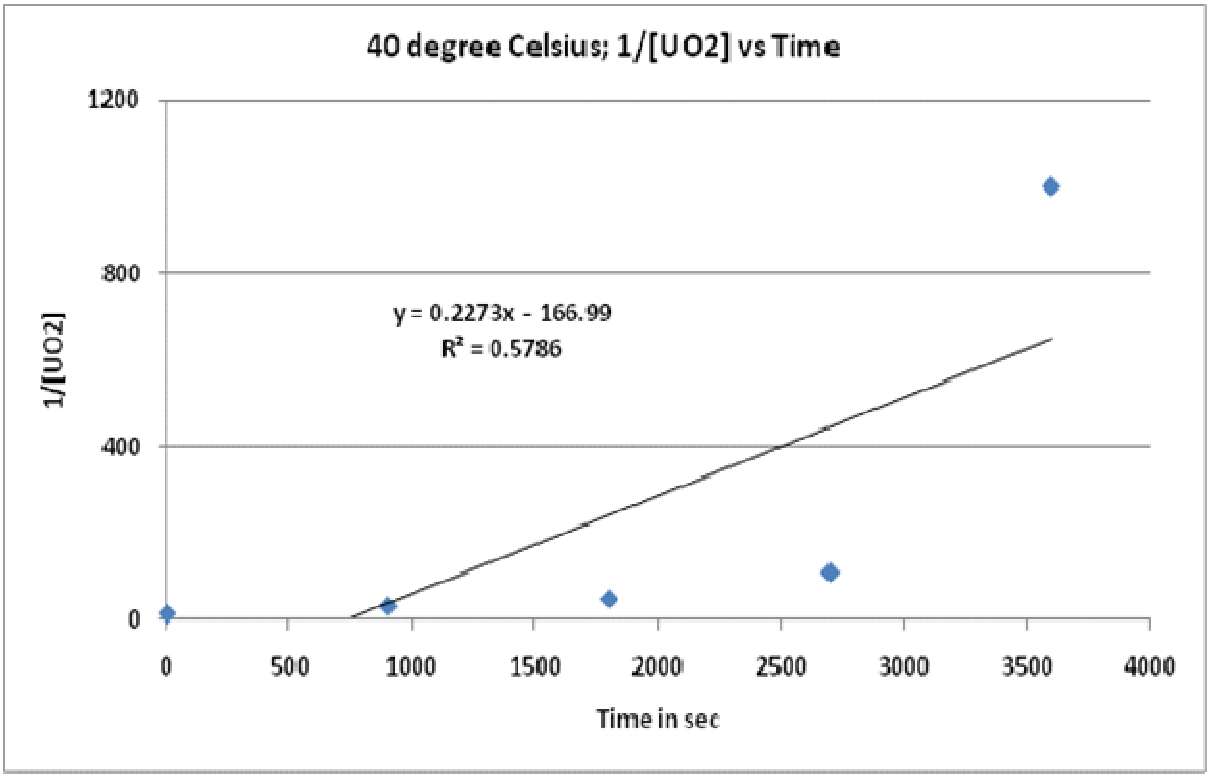


Figure 4-12: Second order plot for 40 °C

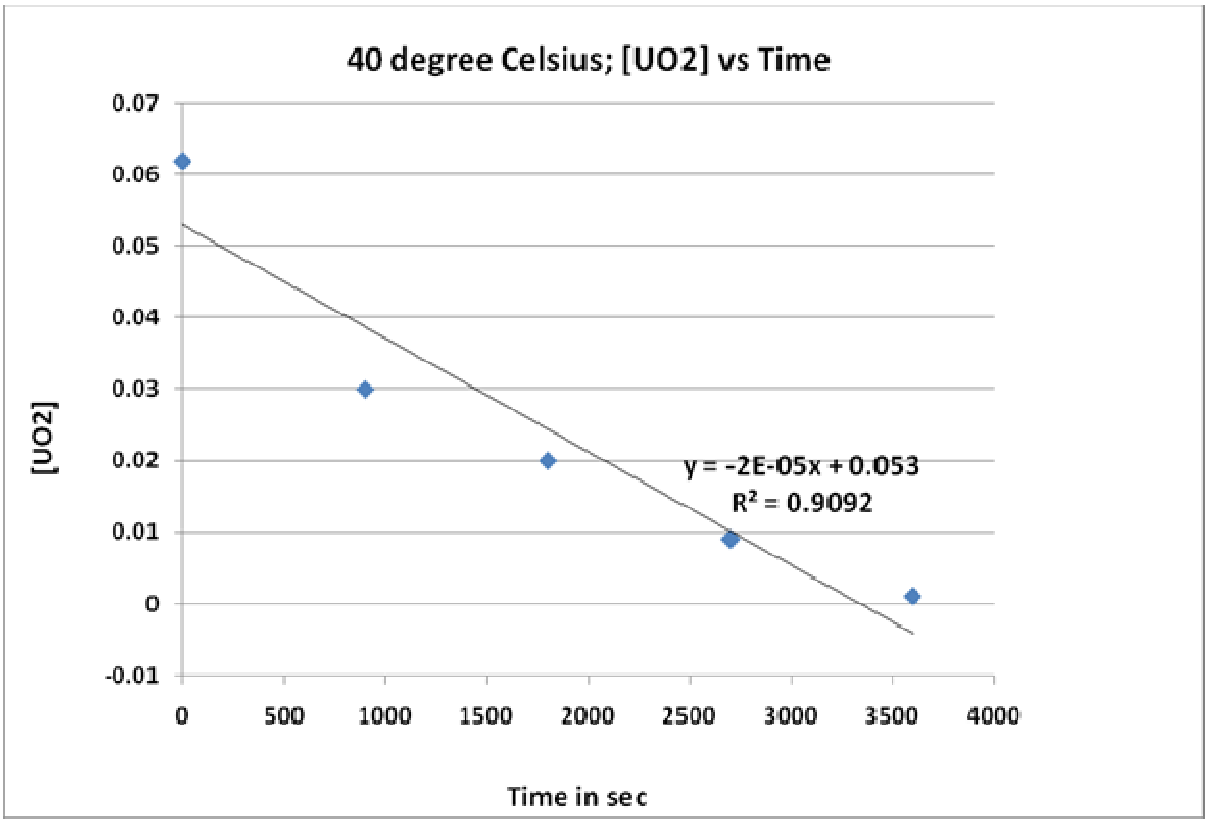


Figure 4-13: Zero order plot for 40 °C

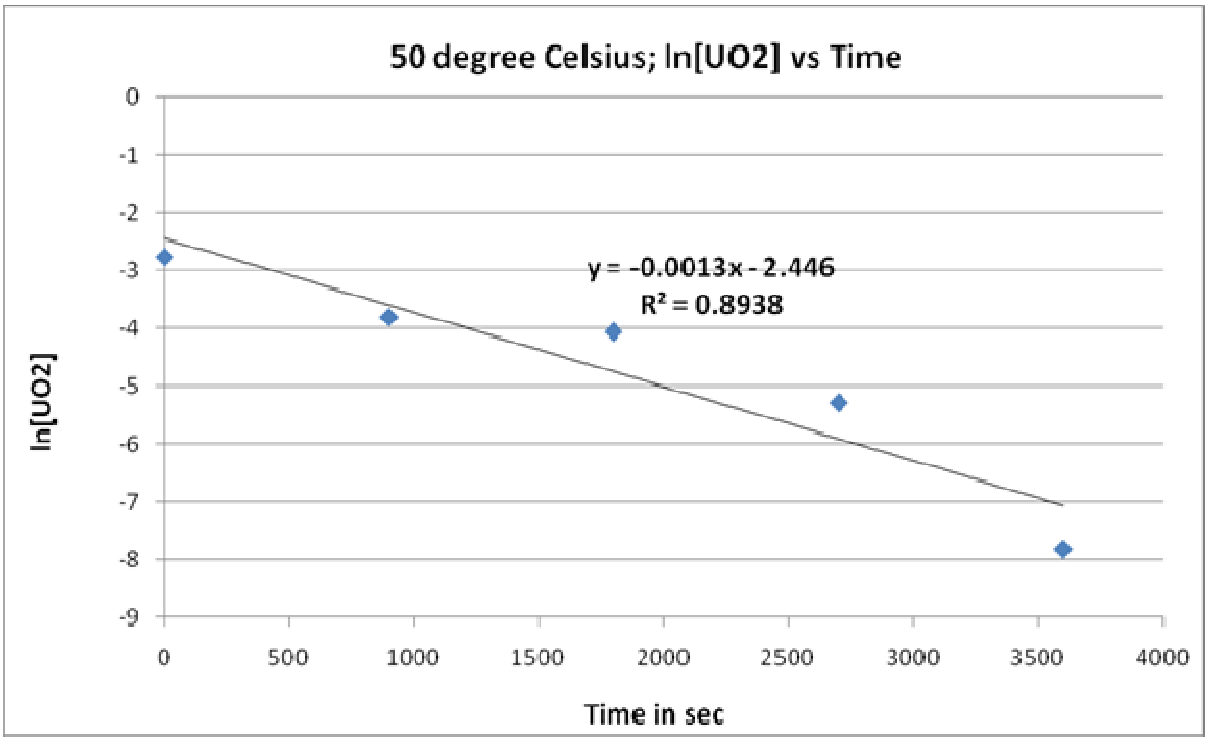


Figure 4-14: First order plot for 50 °C

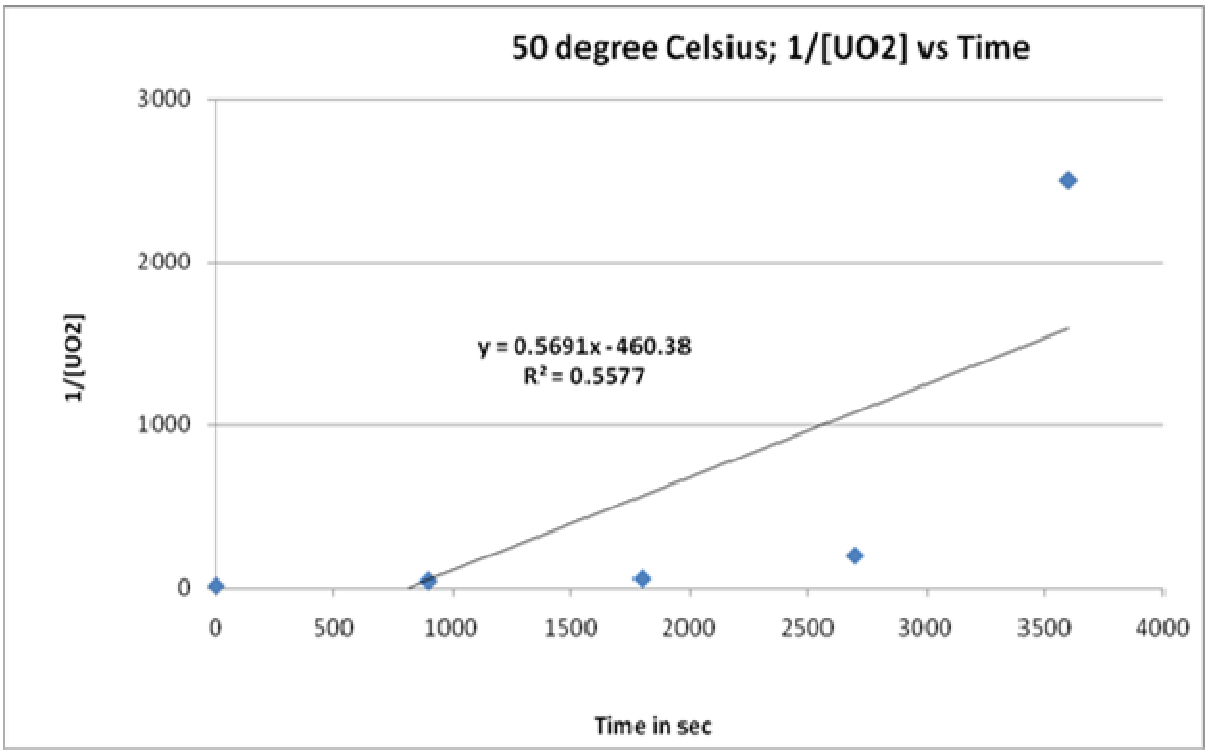


Figure 4-15: Second order plot for 50 ^{o}C

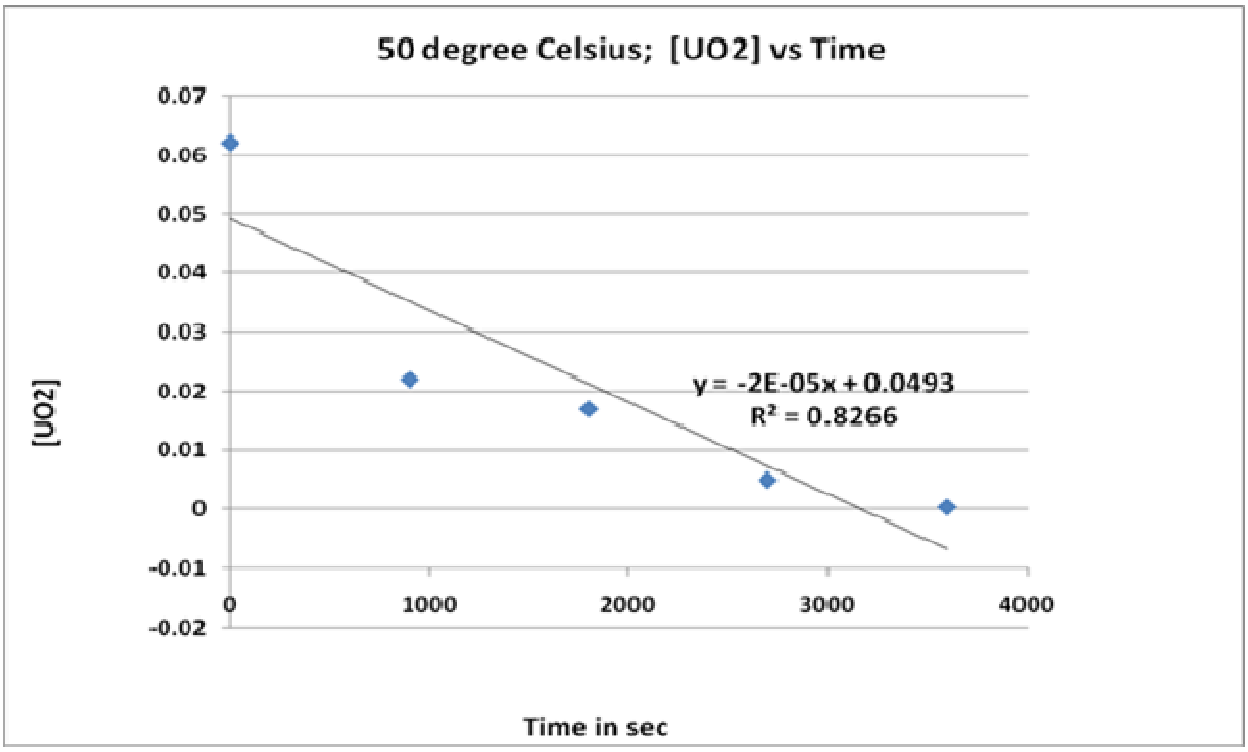


Figure 4-16: Zero order plot for 50 ^{o}C

4.1.5 Rate of decomposition of uranium dioxide

The chemical reaction of uranium dioxide dissolution in solutions of ammonium carbonate and hydrogen peroxide was studied using experiments in which the reactants were charged to a vessel and maintained at constant and uniform temperature.

The change in the amount of uranium dioxide as a function of time, when reaction was performed at 25, 40 and 50 ^{o}C, is given in Tables 24; 25 and 26 (see Appendix 3).

Using these data, the order of the rate law with respect to uranium dioxide concentration was verified by constructing a plot of ln [UO_2] versus time. The value of the rate constant k was determined from the slope of the resultant line.

Since the reaction is first order, the slope of the line equals –k, where

$$\text{Slope} = \frac{\Delta(\ln[UO2])}{\Delta t} = -k \qquad [22]$$

Table 4.1 below show the rate obtained at different temperatures and solid-liquid ratio

Table 4.1: Values of k for different temperatures and solid-liquid ratio

T (^{o}C)	$k_{1/40}$	$k_{1/60}$	$k_{1/80}$	RSD, %
25	0.00035	0.00039	0.00043	10.2
40	0.00108	0.00114	0.00109	2.9
50	0.00132	0.0014	0.0012	7.7

As it can be seen, k increases with temperature but increases slightly with an increase of solid-liquid ratio. Although the values of k vary little with the different solid-liquid ratio investigated, k values obtained at solid liquid-ratio of 1:60 exceed slightly the one obtained with solid-liquid ratio of 1:80 while leaching at 40 ^{o}C and 50 ^{o}C. Thus, leaching at solid-liquid ratio of 1:60 appears to be more advantageous.

4.1.6 Activation energy

In order to obtain the value of the activation energy, ln k was plotted against (1/T), which resulted in a straight line for different solid-liquid ratios used. The values of activation energy and R^2 obtained for each solid-liquid ratio are shown in Table 4.2 below.

It may be seen from these results that there is a trend between the values of activation energy and R square obtained at solid-liquid ratio of 1:40 and 1:60. The activation energy appears to decrease with the increase of solid-liquid ratio moving towards the diffusion controlled region. This is due to the fact that in the more diluted solution, the reaction is likely to be influenced by the reagents concentration then by the temperature used under the conditions investigated. Beside this, the correlation relation for the plot done at solid-liquid ratio of 1:80 was found to be 0.89 and confirms that the relationship between the rate of uranium dioxide dissolution and the temperature is not strong as for the other solid-liquid ratios used.

Table 4.2: values of activation energy and R square at different solid-liquid ratio

S/L ratio	Ea (kJ)	R^2
1/40	44.2	0.94
1/60	42.5	0.94
1/80	33.9	0.89

Table 4.3 shows the values of k at different solid-liquid ratio and temperatures used. The average activation energy was found to be 40.2kJ/mol, which is lower than what was reported in literature as being 57kJ/mol and 51.1kJ/mol respectively by Sharma *et al.* (1996) and du Preez *et al.* (1981). The reason may be that the dissolution process was done in ammonium carbonate and hydrogen peroxide as oxidant in this study, while, sodium carbonate-bicarbonate solutions containing sodium hypochlorite were used in the experiments reported by the above authors.

Table 4.3: Values of ln k at different temperatures and solid-liquid ratio

T (°C)	1000/T	k	ln k 40	ln k 60	ln k 80	Average	RSD %
25	3.355705	0.00035	-7.96	-7.85	-7.75	-7.85	1.31
40	3.194888	0.00108	-6.78	-6.78	-6.82	-6.81	0.42
50	3.095975	0.00132	-6.57	-6.57	-6.73	-6.64	1.17

The temperature dependency of dissolution reactions of uranium dioxide with different solid-liquid ratio characterized by the Arrhenius equation is further shown by Figure 4.17. Thus we see that a plot of average ln k against 1/T gives a straight line.

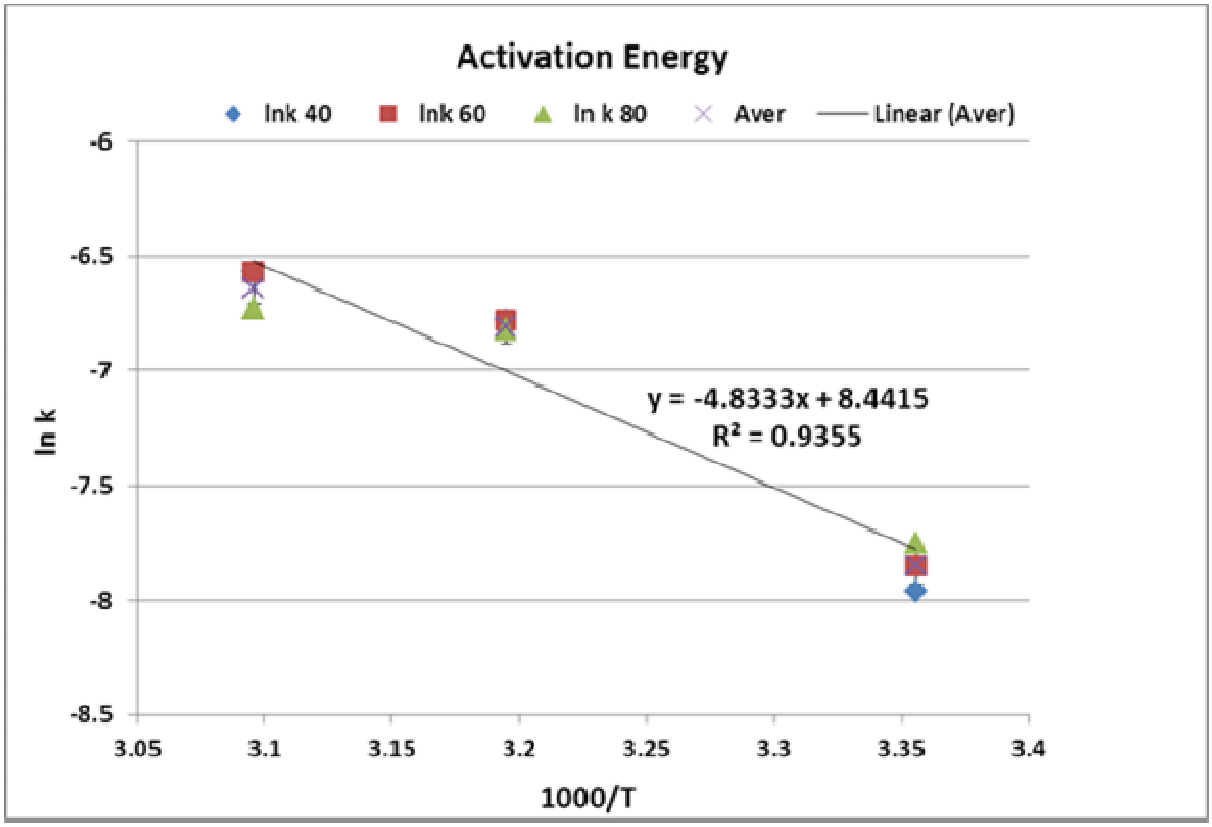


Figure 4-17: Plot of average ln k against 1/T

The correlation relation R^2 for this plot is 0.93 and indicates that there is strong relationship between the rate of uranium dioxide dissolution and the temperature.

Apparent activation energy lower than 20kJ/mol suggests a diffusion controlled process while a value in the range 40-85kJ/mol is indicative of a chemically controlled mechanism. The above activation energy of 40.2kJ/mol is, therefore, in agreement with a chemically controlled process. This agrees with work of Sharma and of du Preez. Thus, as stated above, an increase of reaction temperature is expected to strongly affect uranium dioxide dissolution in the range of conditions investigated.

Results of the investigations based on the determination of the order of reaction with respect to other reagents involved in the dissolution of uranium dioxide are presented in the next section.

4.1.7 Order of reaction for ammonium carbonate and hydrogen peroxide

The order of reaction with respect to hydrogen peroxide (Figure 4.18) and with respect ammonium carbonate (Figure 4.20) was found to be unity at 25 ^{o}C. This is also the case for 50^{o} C where a pseudo-first order reaction with respect to hydrogen peroxide (Figure 4.19) and to ammonium carbonate (Figure 4.21) was found. The data used to plot the following graphs are tabled in Appendix 3.

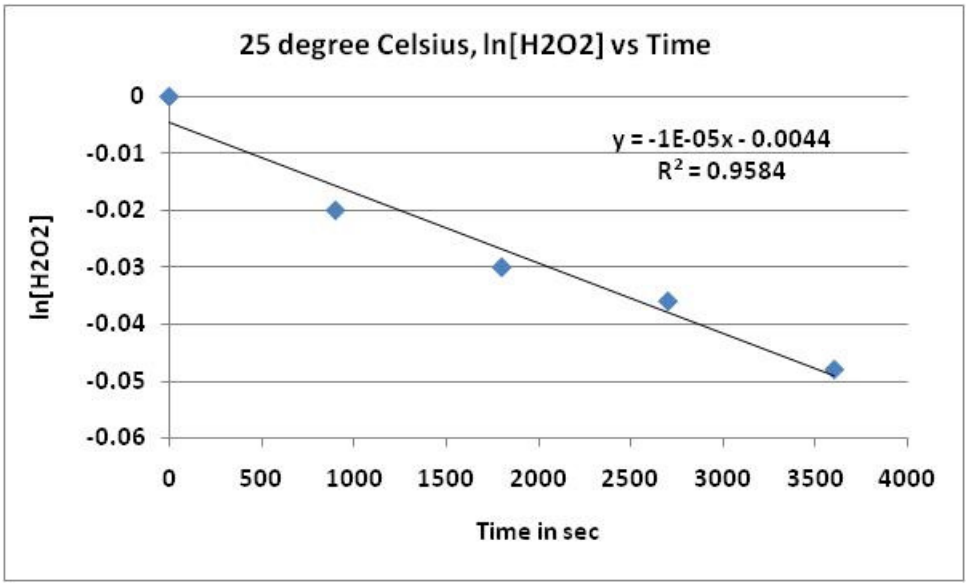


Figure 4-18: First order plot with respect to H_2O_2 at 25 ^{o}C

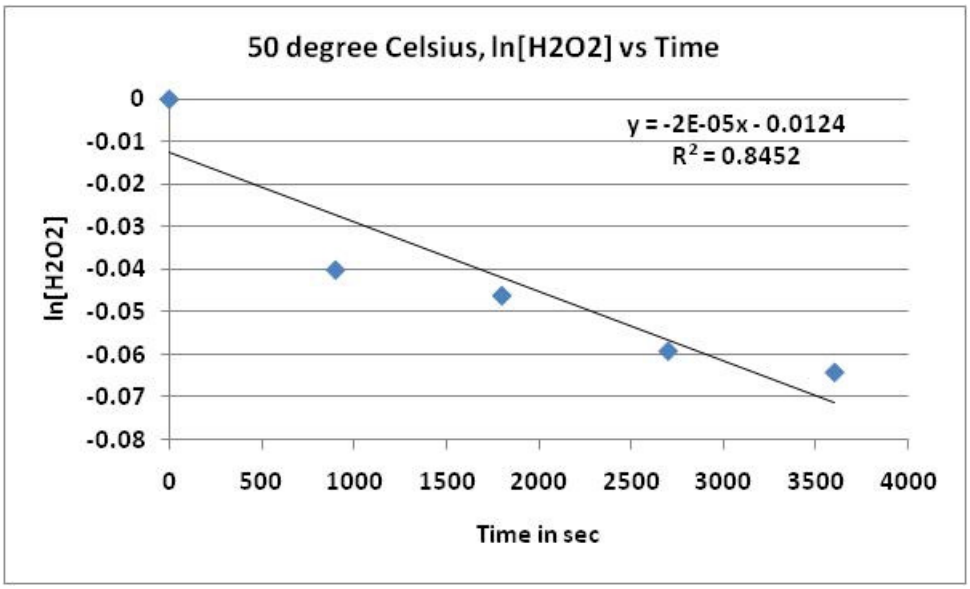


Figure 4-19: First order plot with respect to H_2O_2 at 50 °C

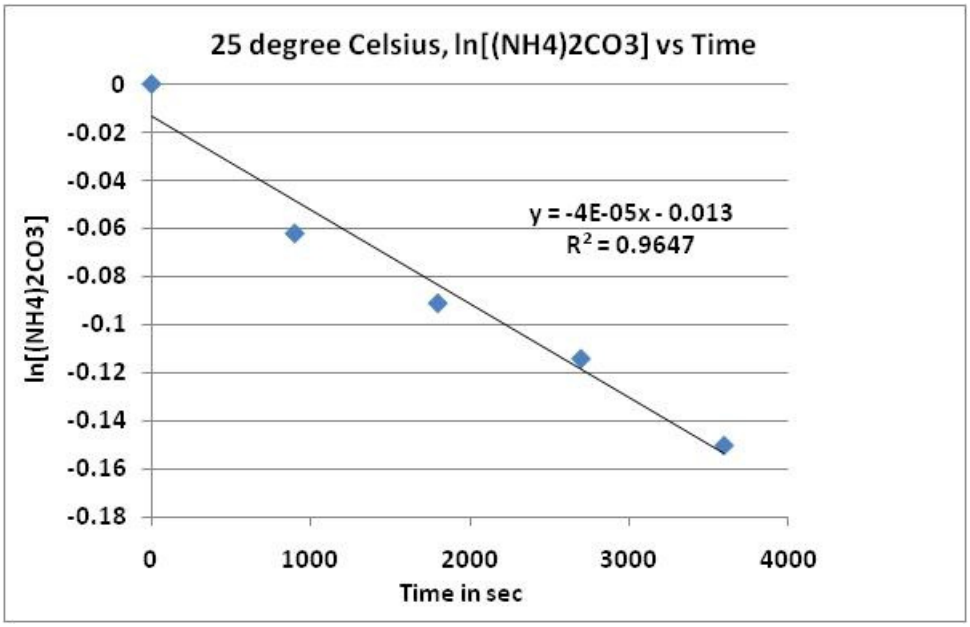


Figure 4-20: First order plot with respect to $(NH4)_2CO_3$ at 25 °C

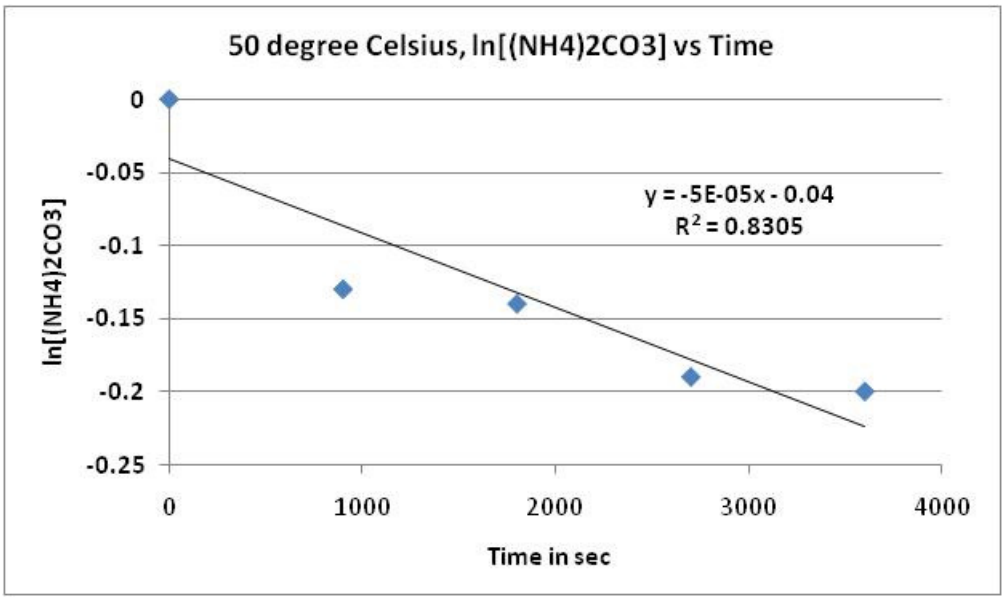


Figure 4-21: First order plot with respect to $(NH4)_2CO_3$ at 50 ºC

4.2 Dissolution of simulated residue

The simulated residue has been stated to contain uranium in a mixture of oxidation states, predominantly in a U(IV) oxidation states. Thus, the knowledge of the data of dissolution of pure uranium dioxide, as presented in Section 4.1, was essential for the dissolution of the uranium residue. The following investigations were carried to compare the dissolution kinetics of the pure uranium dioxide and the uranium residue. This comparison was made from the obtained data of pure uranium dioxide dissolution at 50 ^{o}C. Besides this, the effect of different cations on the dissolution of the simulated residue was also investigated.

4.2.1 Dissolution in solutions of sodium carbonate and bi-carbonate

The dissolution of the simulated residue in sodium carbonate-bicarbonate solutions containing hydrogen peroxide as an oxidant was investigated at the temperature of 60 ^{o}C. Experimental parameters included variable dissolution time, hydrogen peroxide and total carbonate concentrations. For a total carbonate concentration of 0.5 M, the sodium carbonate/bicarbonate ratio was adjusted to obtain a solution pH of 9.0, and for 1 M it was 10.0.

Figure 4.22 and Figure 4.23 below illustrate the impact of various concentrations of hydrogen peroxide on the dissolution of 0.5 g of simulated residue in sodium carbonate-bicarbonate solutions at pH 9 and 10.

Extensive dissolution of the residue in solutions with no hydrogen peroxide shows that some of the uranium contained in the simulated residue is in oxidation state VI.

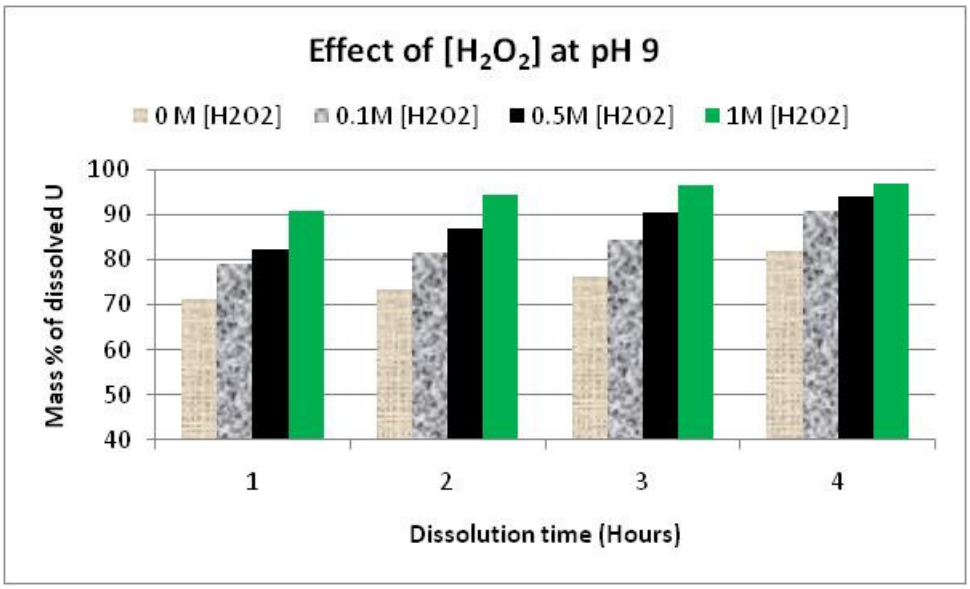


Figure 4-22: Effect of various hydrogen peroxide concentrations on simulated uranium residue dissolution at pH 9

From the results shown in the above figures, it is seen that the mass % of uranium dissolved increases as the concentration of hydrogen peroxide is increased from 0.1 M to 1 M. This is likely due to the combined effects of the oxidative potential of hydrogen peroxide in addition to the complexation of uranium (VI) with carbonate to form a mixed peroxo – carbonato complex.

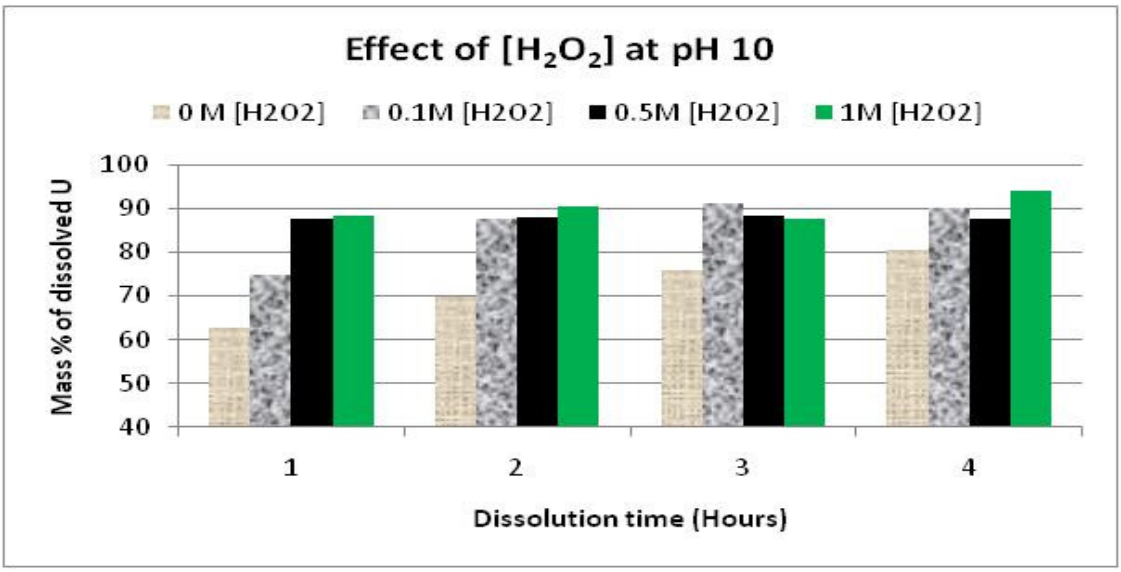


Figure 4-23: Effect of various hydrogen peroxide concentrations on simulated uranium residue dissolution at pH 10

4.2.2 Pressure leaching of uranium residue

0.5 g of uranium residue was added into 30 ml of 1 M ammonium carbonate solution (pH 9.2) or sodium carbonate/bicarbonate solution. 3 ml of hydrogen peroxide 30% were added into the solution for the experiments done without oxygen gas. The oxygen pressure was maintained at 400kPa for the experiments run without hydrogen peroxide.

The rate of uranium dissolution was found to be lower in the leaching experiments done without hydrogen peroxide. Figure 4.24 and Figure 4.25 illustrate the comparison between the impact of oxygen gas and hydrogen peroxide on the dissolution of uranium.

On average more than 90% of uranium was dissolved after 3 hours of leaching with hydrogen peroxide at 60 ^{o}C while 86% of uranium was dissolved when using oxygen gas. It is seen that, in sodium carbonate solution, the dissolution rate becomes very slow after 1 hour of leaching with oxygen, while a decrease in dissolution rate is also observed after 1 hour while leaching with hydrogen peroxide.

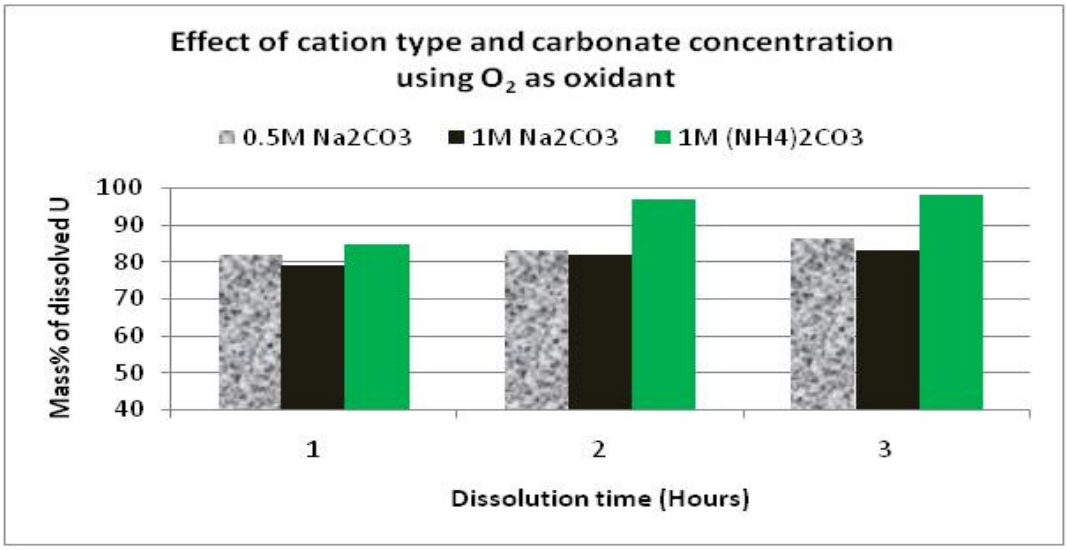


Figure 4-24: Comparison of uranium dissolution rates using different cations and carbonate concentrations with oxygen gas at 400 kPa, 60 ^{o}C

From the results shown in Figure 4.24 and Figure 4.25, it is observed that faster dissolution of the residue occurs when leaching with hydrogen peroxide as an oxidant than with oxygen gas: 99% uranium is extracted from the residue after 60 minutes while leaching with hydrogen peroxide; almost two hours are needed to achieve the same extent in the presence

of oxygen at the same temperature. Maybe the difference would probably be less noticeable under conditions where oxygen is continually sparged into the leach slurry, especially if it is ensured that there is adequate contact between the gaseous and solution phases.

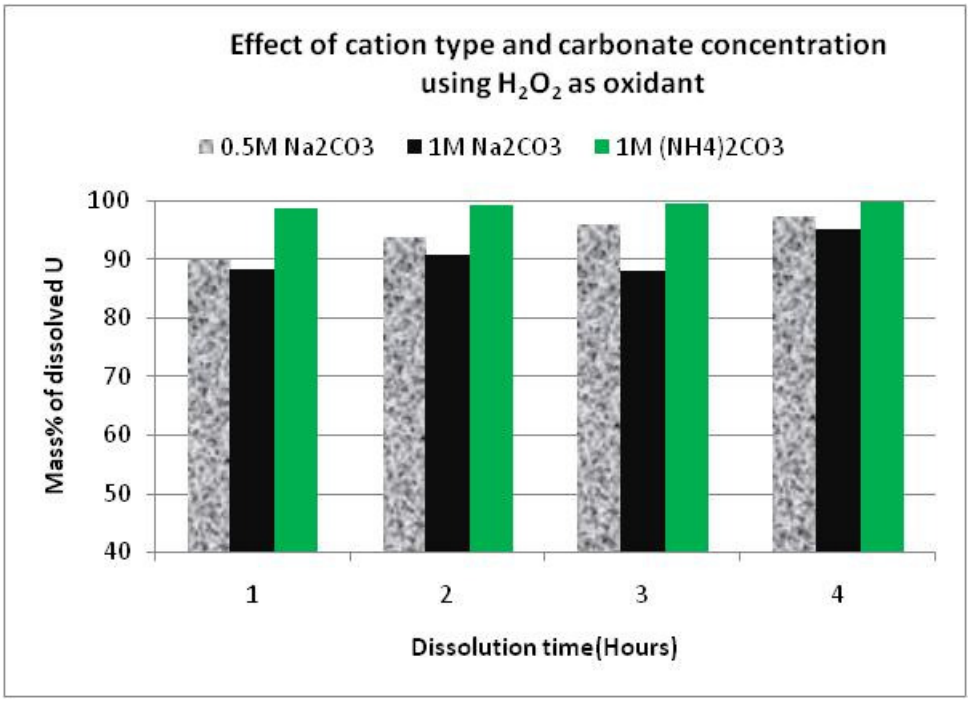


Figure 4-25: Comparison of uranium dissolution rates using different cations and carbonate concentrations with 1 M (mol/l) hydrogen peroxide, 60 ^{o}C

The above leaching tests have indicated that a greater extent of uranium extraction occurs in ammonium carbonate solutions than in sodium/bicarbonate solutions when using the same amount of hydrogen peroxide or oxygen gas (see Figure 4.24 and Figure 4.25). More than 98% of uranium was dissolved after 1 hour of leaching in 1 M hydrogen peroxide at 60 ^{o}C while 3 hours of leaching were needed to dissolve 88% and 96% of uranium in sodium carbonate-bicarbonate solutions (pH 10 and 9) under identical reaction conditions.

The plots of the uranium dissolution *vs* time at different hydrogen peroxide concentrations are given in Figure 4.26. It was found that dissolution extent of uranium extraction increased with the reaction time and hydrogen peroxide concentrations. At 60 ^{o}C within 60 minutes, only 62% of the uranium particles dissolved when the concentration of hydrogen peroxide was 0.1 M; the value increased considerably to almost 99% when the concentration of hydrogen peroxide rose to 1 M.

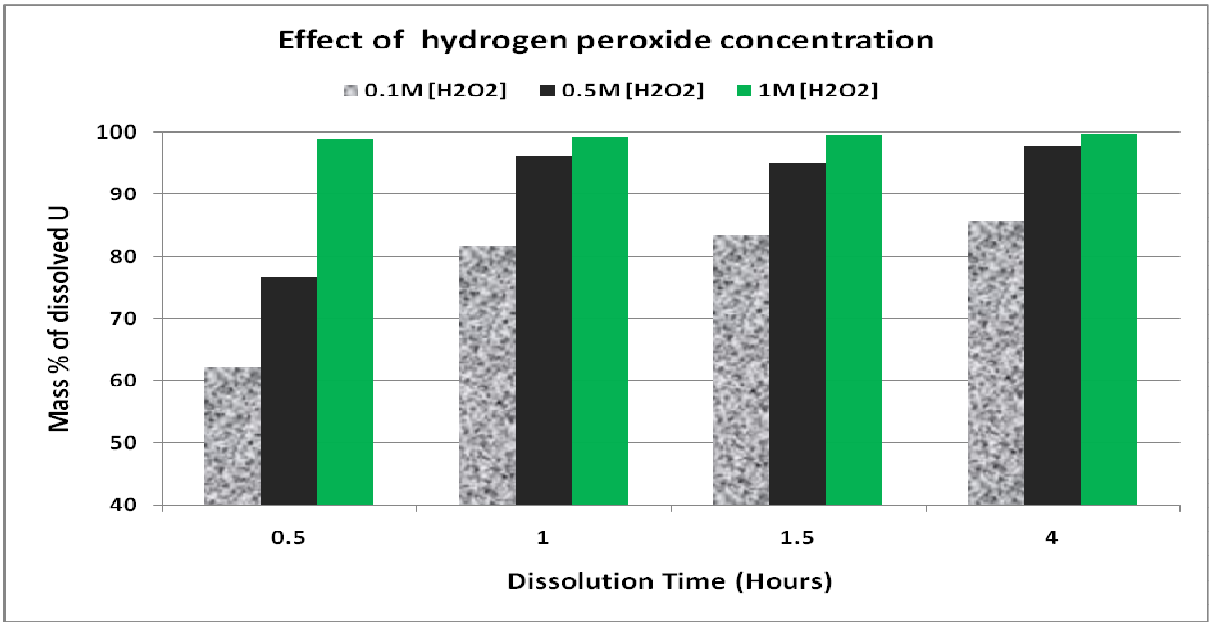


Figure 4-26: Effect of hydrogen peroxide concentration on uranium dissolution rate in 1 M ammonium carbonate solution, 60 ^{o}C

Initial leaching of the uranium contained in the residue is quite rapid, with about 98% recovery indicated after 30 minutes as shown in Figure 4.26 above. This effect confirms that uranium contained in the residue easily dissolves in 1M ammonium carbonate and 1 M hydrogen peroxide solutions forming orange mixed carbonate-peroxide complexes. The pH of 1 M ammonium carbonate and hydrogen peroxide solution is about 8.5 at which stable peroxide-carbonate uranyl complexes exist.

The reaction temperature was shown to have some effect, as may be seen in Figure 4.27 below. The experimental results show that the dissolution of uranium increased with the increase in temperature. Only 63% of the uranium dissolved in 1 M ammonium carbonate and 1 M hydrogen peroxide solution at 25 ^{o}C, during the first 30 minutes. However, when the temperature was increased to 60 ^{o}C, the dissolution increased to almost 99%.

It may be seen that the leaching reaction is no longer under kinetic control at temperatures of 50 ^{o}C and above. This is in agreement with the trends seen above for differing sodium carbonate concentrations and ammonium carbonate concentrations at a reaction temperature of 60 ^{o}C. With hydrogen peroxide at 1 M as oxidant, under the conditions used here, the

reaction is fast and almost complete after 30 minutes. At lower hydrogen peroxide concentrations the reaction is slower, as may be seen in Figure 4.26.

At the low concentrations of 0.1 M and 0.5 M hydrogen peroxide, the leaching rate slows considerably after 1 hour. Futher dissolution is probably dependent on the dissolution of air oxygen in the lixiviant, and is thus slow.

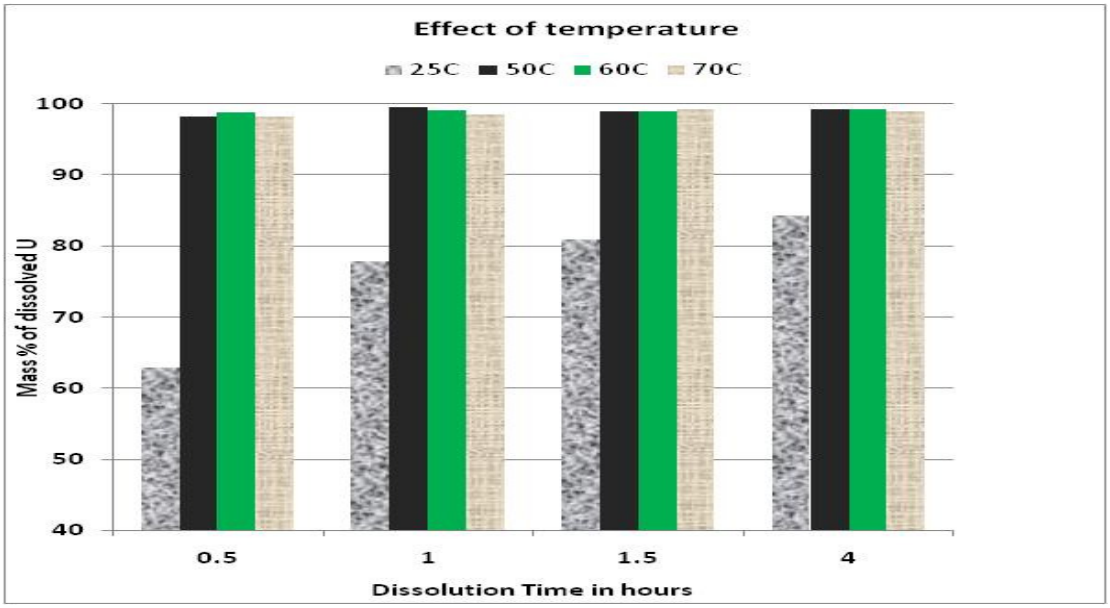


Figure 4-27: Effect of various temperatures on uranium residue dissolution rate in 1 M ammonium carbonate with 1 M hydrogen peroxide

From all the results obtained above, it is clear that high extractions of uranium can be attained in 1 hour at 60 ^{o}C.

4.3 Uranium residue leach kinetics

4.3.1 Rate law for dissolution

As outlined in Section 4.2.1, it was found that uranium (VI) contained in the uranium residue leaches quickly. Thus, kinetics study of the residue was done taking into consideration only the amount of the dissolved uranium (IV). The aim was to check if the reaction orders are the same with what was obtained for pure uranium dioxide, ammonium carbonate and hydrogen peroxide. Data used to plot the following graphs are found in Appendix 4.

Figure 4.28 shows graphically a first order reaction while Figure 4.29 illustrates a pseudo-first order reaction. This implies that the dissolution of uranium residue is first order, as shown by the linearity of the graph $\ln[UO_2]$ versus time.

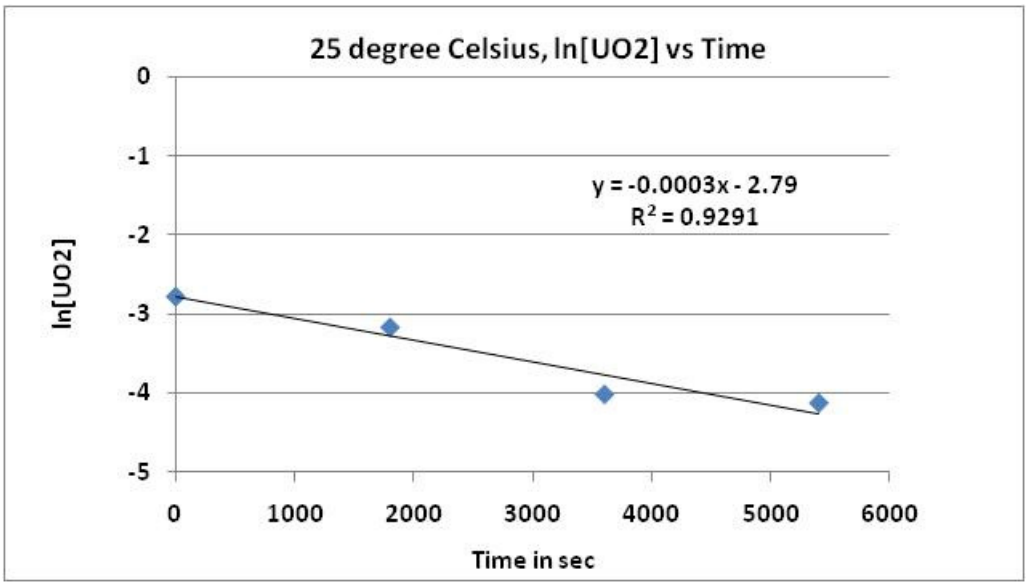


Figure 4-28: First order plot for 25 ^{o}C

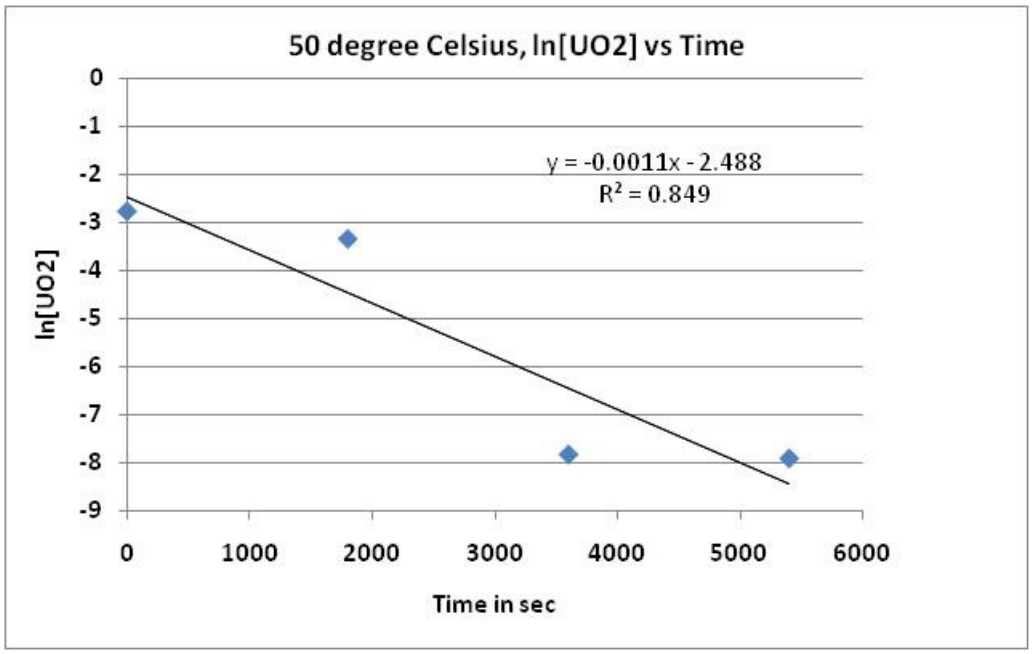


Figure 4-29: First order plot for 50 ^{o}C

The order of the reaction was found to be also unity with respect to hydrogen peroxide and ammonium carbonate respectively (see Figure 4.30, Figure 4.31 and Figure 4.32 and Figure 4.33 below).

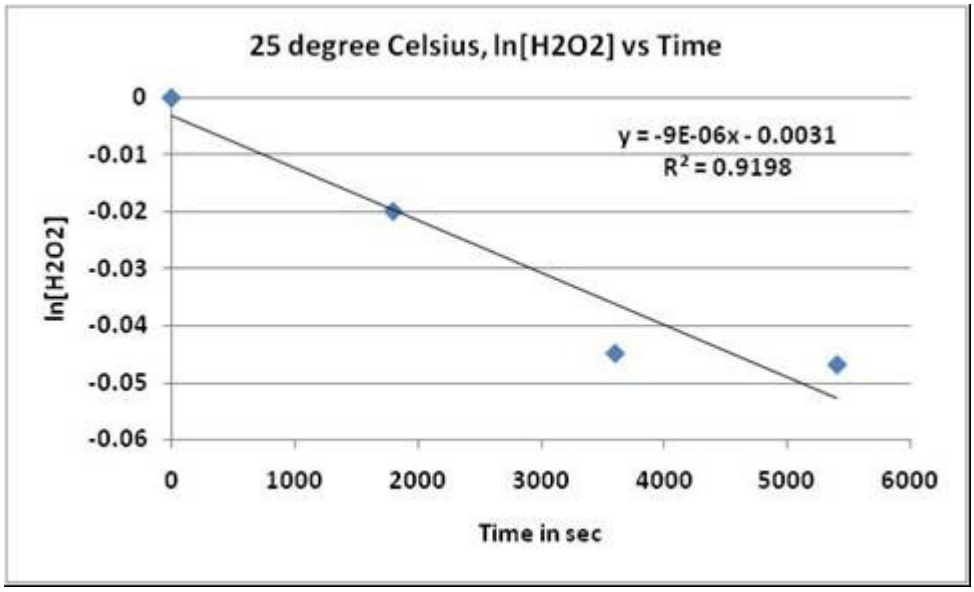


Figure 4-30: First order plot with respect to H_2O_2 at 25 ^{o}C

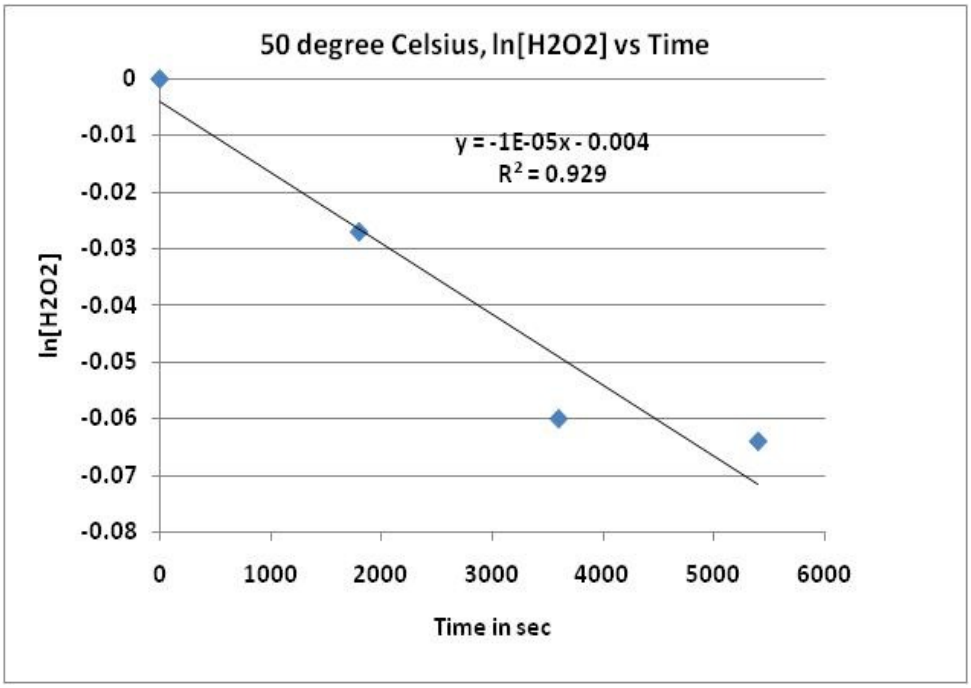


Figure 4-31: First order plot with respect to H_2O_2 at 50 ^oC

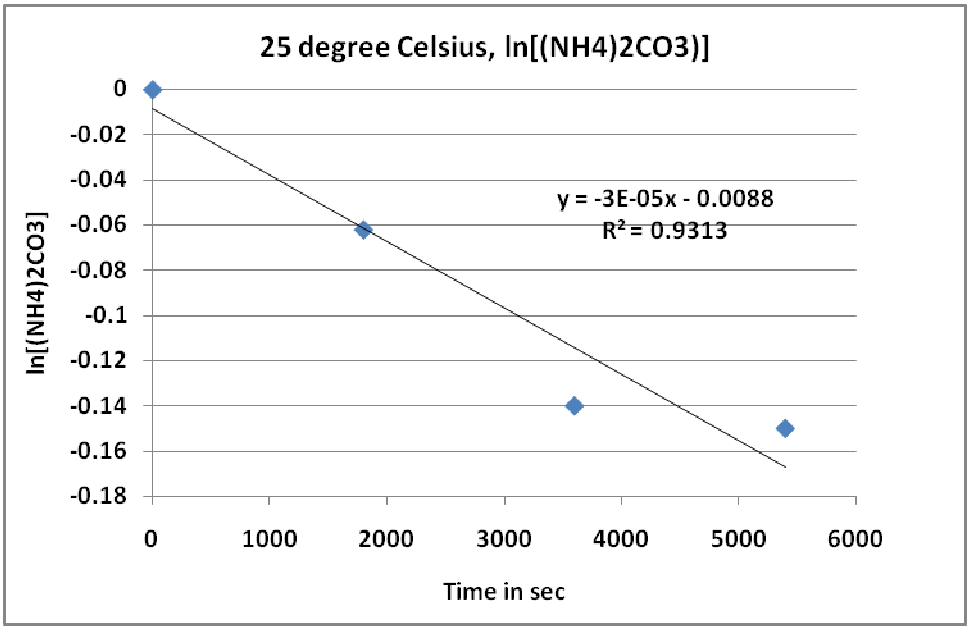


Figure 4-32: First order plot with respect to $(NH_4)_2CO_3$ at 25 ^oC

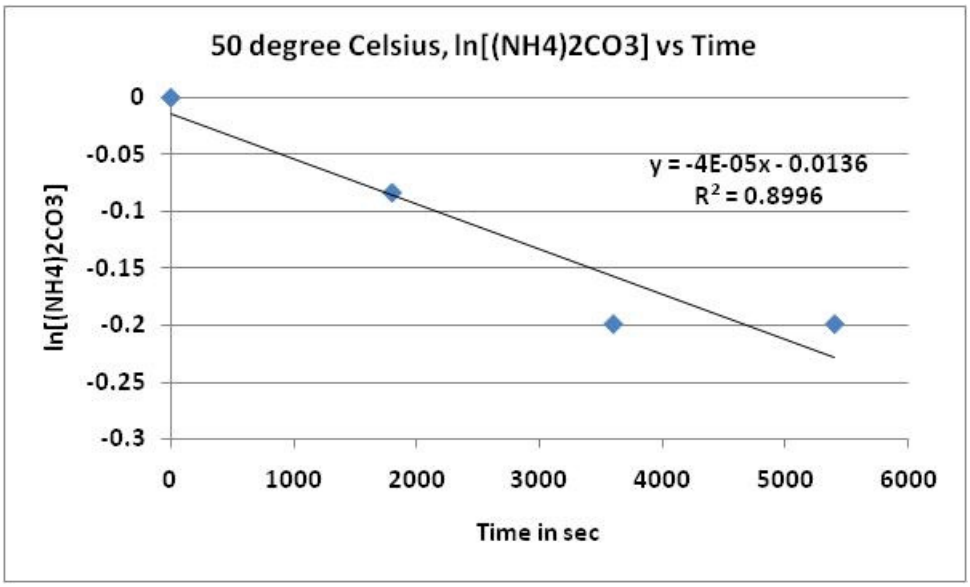


Figure 4-33: First order plot with respect to $(NH_4)_2CO_3$ at 50 ^oC

4.3.2 Activation energy for uranium residue dissolution

From the values given in Table 4.3 below, the rate constant goes on increasing as the temperature goes up from 25 ^oC to 60 ^oC. However, slight increases of the rate of reaction was observed by raising the temperature just a little bit, from 50 to 60 ^oC. Thus, the rate of increase falls off quite rapidly above 50 ^oC.

Table 4.3: Values of k for uranium residue dissolution at various temperatures

T(^{o}K)	1000/T	k	ln k
298	3.355705	0.00025	-8.3
323	3.095975	0.00095	-6.96
333	3.003003	0.00098	-6.93

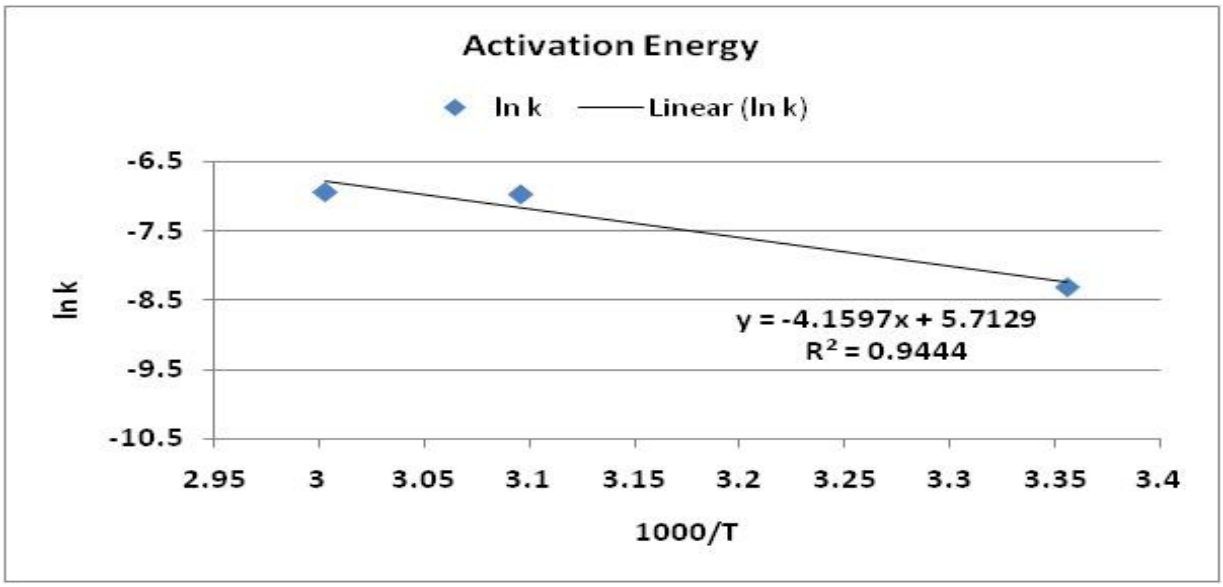


Figure 4-34: Plot of ln k against 1/T for uranium residue dissolution

It can be seen, from the above figure, that the kinetics of the uranium (IV) in the residue is similar to the one for pure uranium dioxide. Besides this, the activation energy was found to be 45.5kJ/mol (chemically controled process), which is above the activation energy found for pure uranium dioxide dissolution (40.2kJ/mol) under the same experimental conditions.

5. RECOVERY OF URANIUM

5.1 Introduction

The recovery of uranium is an essential step in its re-use. The Pourbaix diagram shows that the uranyl carbonate complex ion is stable up to a pH of 13. Thus ammonia cannot be used as base in order to recover uranium from the leach solutions. A strong base such as sodium hydroxide would have to be used. This would, however, introduce unwanted sodium ions into the solution. The leach solution could be acidified to a pH below 6 in order to precipitate the uranyl values as a carbonate. A similar objection arises: using any commercial acid would introduce unwanted anions such as sulphate or chloride, which will form soluble complexes with the uranyl ion.

To recover uranium from the ammonium carbonate leach solutions the process of steam stripping to precipitate the uranium as schoepite ($UO_3.2H_2O$) is thus the best solution (Merritt, 1971). To use the steam stripping, the temperature of the pregnant eluate must be raised to the boiling point by injecting live steam into the solution. As the steam condenses, it releases energy and the temperature rises.

In the case of ammonium uranyl tri-carbonate leach solution, an increase of the temperature above 65^{o} C will cause the complex to dissociate (Robert *et al.*, 1981). Carbonate then volatilizes as carbon dioxide and ammonia is released as ammonia:

$$(NH_4)_2CO_3 = 2\ NH_3 + CO_2 + H_2O \qquad [23]$$

Carbonate dioxide and ammonia can be recovered for reconstituting the lixiviant in a closed process. Temperature remains the factor determining the rate of reaction since increasing temperature affects the evaporation of ammonia and carbon dioxide. Thus, the rate at which steam is injected has to be taken into account. The pH also plays an important role as the uranyl complex is stable at high pH values (9-11); the pH will decrease due to the loss of ammonia.

Experimentally, it has been found that the precipitate obtained by a simulated stripping process is extremely fine, which makes it difficult to settle or filter. Thus, the aim of this work was to study the possibility to obtain a coarser precipitate from uranyl ammonium carbonate solution using simulated steam stripping.

5.2 Precipitation tests

5.2.1 Precipitation procedure

As stated above, the laboratory was not equipped for steam stripping as done in industry to recover uranium. The process was thus simulated by heating the pregnant liquor on a laboratory stirrer/heater unit.

100 ml of ammonium uranyl carbonate solution of an appropriate initial uranium concentration was heated to 90 ^{o}C with constant stirring (250 rpm) for a certain time. In total 80 ml of water was added bit by bit, for each run to keep the initial volume constant. The heating was stopped once there was no more release of carbon dioxide and ammonia.

5.2.2 Preliminary tests

Preliminary uranium precipitation tests were done using solutions with a pregnant head grade of 84 g/l. The aim of these precipitation tests was to explore the possibility of direct formation of a coarser uranium precipitate by simulated steam stripping at different temperatures.

Precipitation of uranium was observed when heating the solutions at 90 ^{o}C after 1 hour. Precipitation of yellow cake was seen to commence after about 15 minutes. However, the precipitate obtained was very fine grained and difficult to filter. The pH of the solution decreased from pH 9.1 to pH 6.2, with uranium starting to precipitate from pH 7.8. The pregnant head grade dropped to 3 g/l (Figure 5.1). This was confirmed with the change in colour of the solution from red orange to yellow. After resting the mixture for more than 4 hours, it was observed that the liquid above the settled bed was cloudy and still contained fine particles (Figure 5.2).

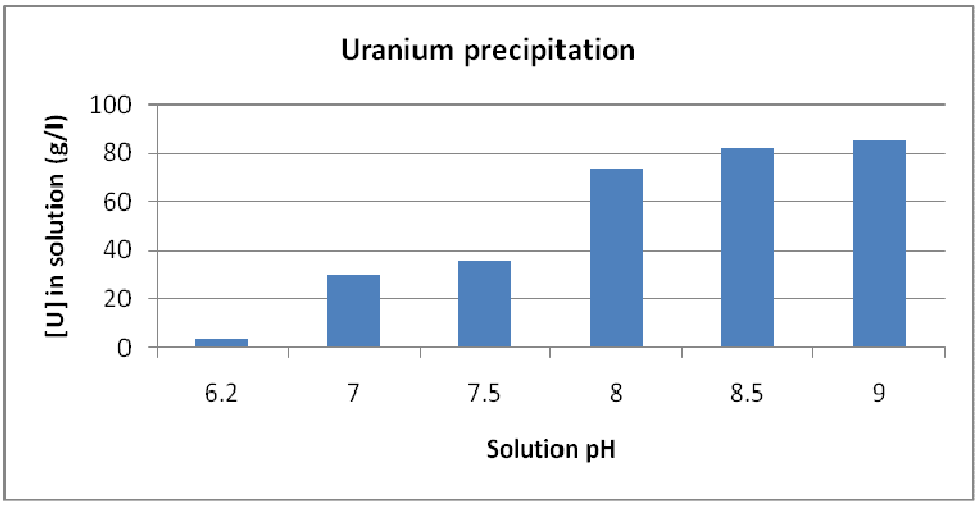
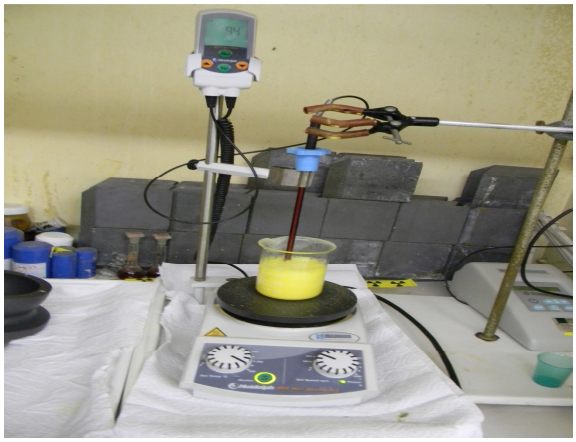


Figure 5-1: Uranium precipitation vs pH



a **b**

Figure 5-2: a) Uranium precipitation and b) Uranium precipitate

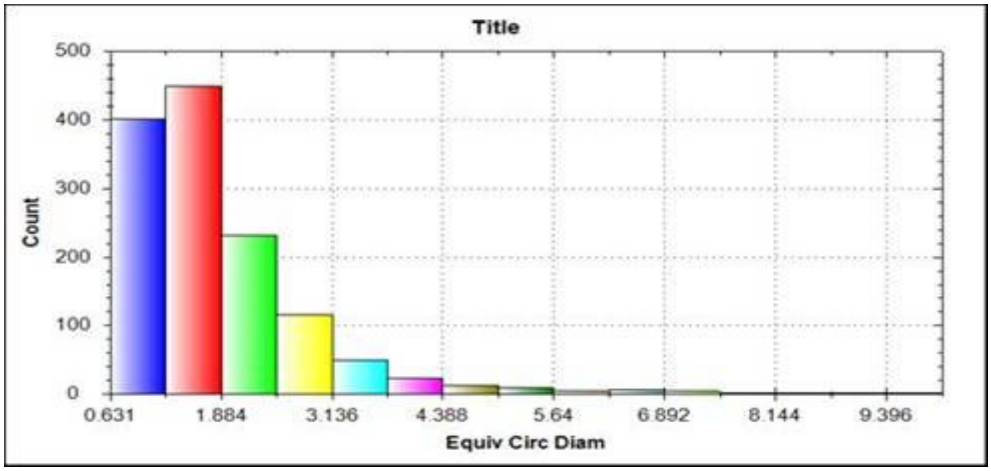


Figure 5-3 : Particle size (µm) distribution obtained for stripping product, no additions

To achieve a coarser precipitate, it was decided to:

- Add 1 g of seed once the precipitate starts forming
- Or dilute the solutions prior to precipitation process: this could help to avoid small size crystallite formation.
- Decrease the rate of agitation from 750 rpm to 250 rpm
- Keep precipitating at higher temperature (90 ^{o}C)

The above conditions were not applied for all the following tests.

5.2.3 Seeding tests

Seeding experiments using U_3O_8 as seed did not result in the formation of a coarser precipitate as expected and the precipitate obtained was green in colour and difficult to filter (Figure 5.4 and Figure 5.5).

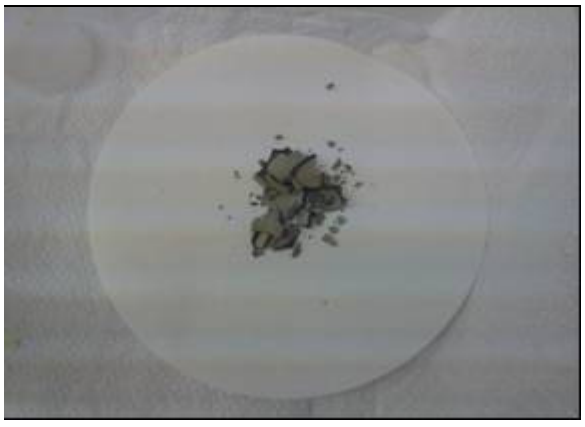


Figure 5-4: Dried precipitate obtained with U_3O_8 seed

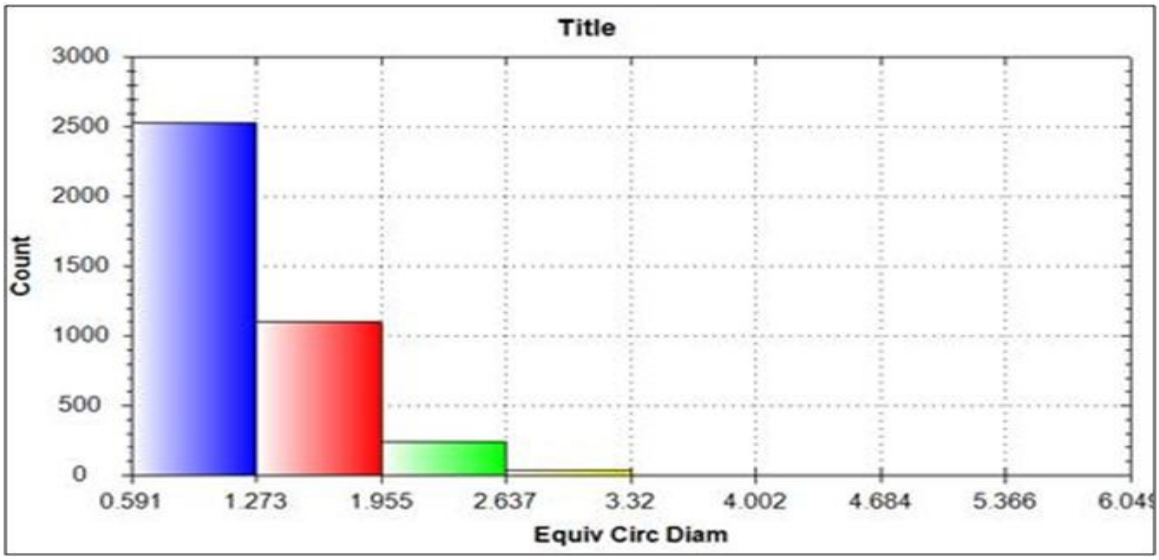


Figure 5-5: Particle size (µm) distribution obtained for stripping product, using U_3O_8 as seed

When UO_2 particles were used as seed, the precipitate was found to settle rapidly and filtration was fast. The processed image and particle size distribution is shown in Figures 5.6 and 5.7.

Although the particles were still very fine, the precipitate was coarser. However, using UO_2 as seed is not ideal as it dilutes the enrichment.

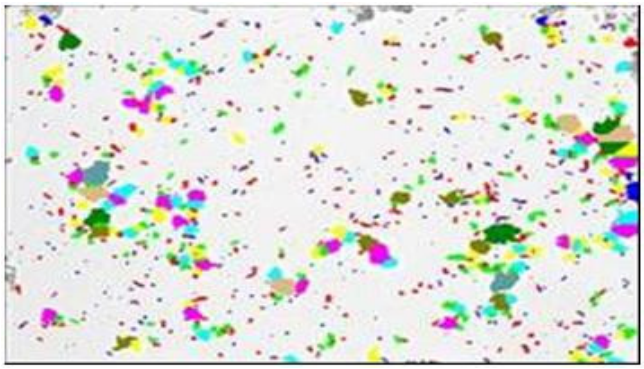


Figure 5-6: Processed images obtained for stripping product, using UO_2 as seed

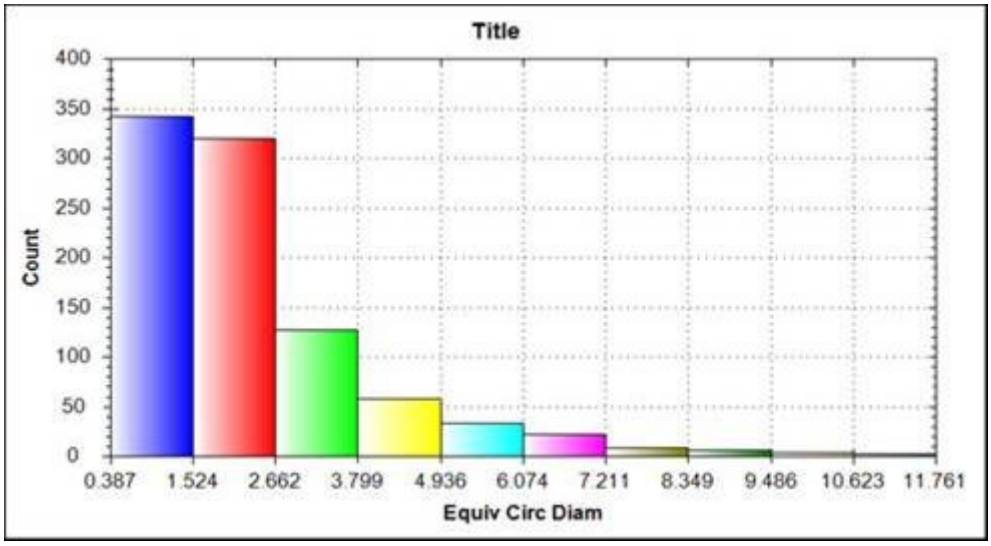


Figure 5-7: Particle size (µm) distribution obtained for stripping product, using UO_2 as seed

Besides this, it was found that the initial uranium concentration used during the above test was too high compared to the one required by the process: the initial uranium concentration must be within the range of 15-20 g/l. Thus, another set of uranyl ammonium carbonate leach solutions having initial uranium concentrations of 17 g/l; 25 g/l; 30 g/l and 45 g/l were prepared accordingly for uranium recovery tests.

5.2.4 Effect of initial uranium concentration

The uranium precipitate obtained with simulated steam stripping of uranyl ammonium carbonate solution having initial uranium concentrations in the range of 15-20 g/l was found to be extremely fine and difficult to filter. This may be due to the solid/liquid interfacial tension and there is a possibility of particles repel due to their surface electric potential. It was then decided to test the effect of non-ionic surfactants.

Non-ionic surfactants are often used to enhance the wetting ability of an aqueous solution. They can change the interfacial tension and affect the kinetics of precipitation by modifying the crystal growth process. Triton x100 and Tween 80 were used separately as surfactants in

this investigation. One drop of each surfactant was added into solution and results are shown in figure 5.8 and figure 5.9 below

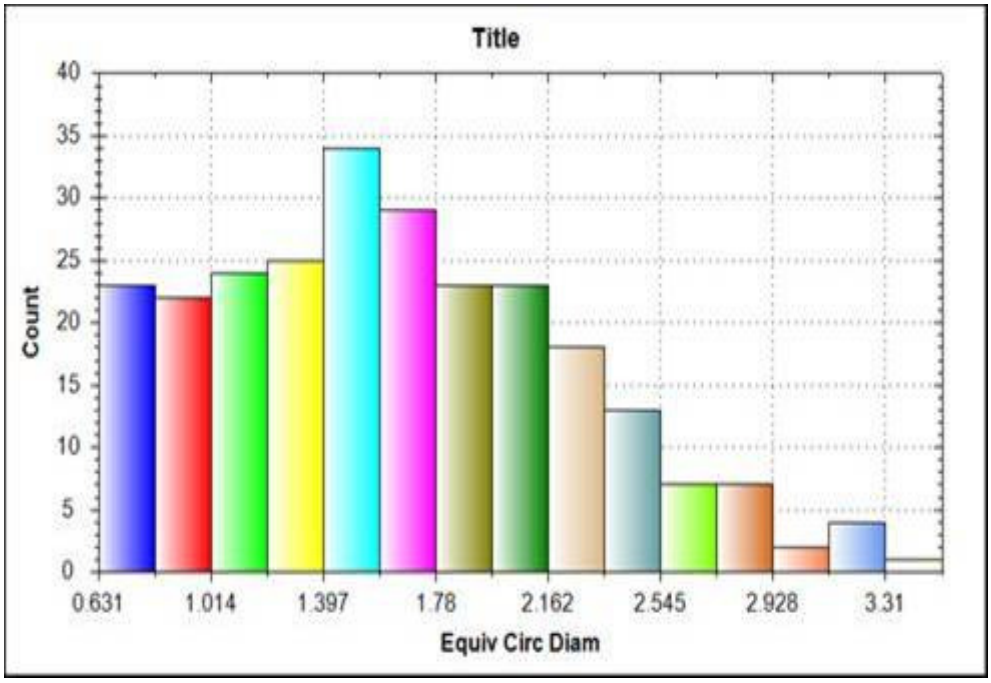


Figure 5-8: Particle size (µm) distribution obtained for stripping product, using triton X 100 as surfactant

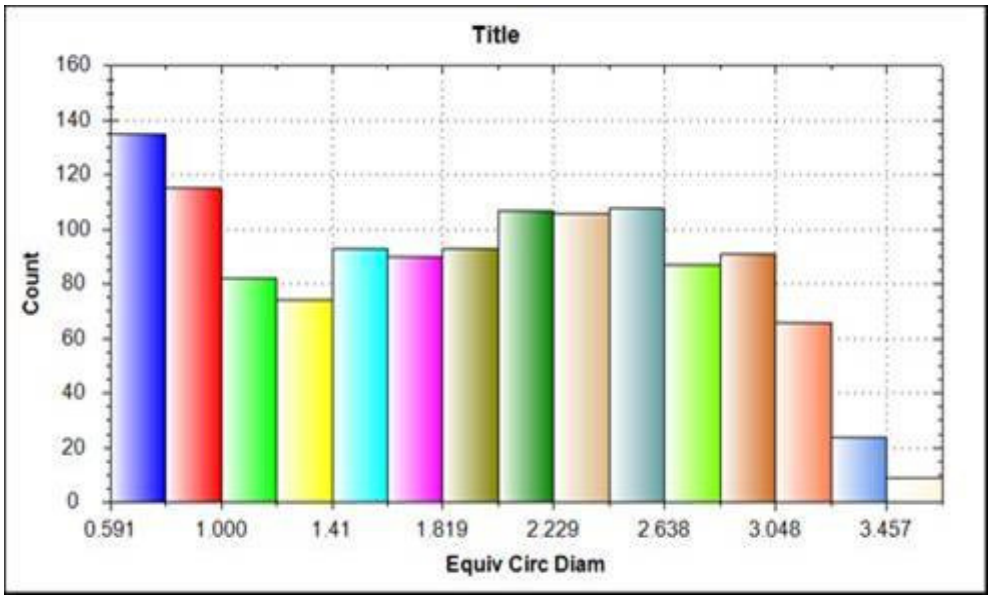


Figure 5-9: Particle size (µm) distribution obtained for stripping product, using Tween 80 as surfactant

The precipitates obtained with the different surfactants did settle fast and were easy to filter. Both surfactants significantly improved the particle size distribution, resulting in about 20% < 1µm.Whereas about 70% was below 1µm in the absence of surfactant or seed. Tween gives larger particles generally (d80 is about 2.4 micron, while Triton gives about 1.8 micron). Tween is the better reagent.

Surfactants have a positive impact on the settling time and filtration of uranium precipitate. However, the precipitate obtained was very hard.

On the other hand, it was found that when precipitation is done from more concentrated solutions, larger particles are obtained without the addition of seed or surfactant, as shown below (Figure 5.10).

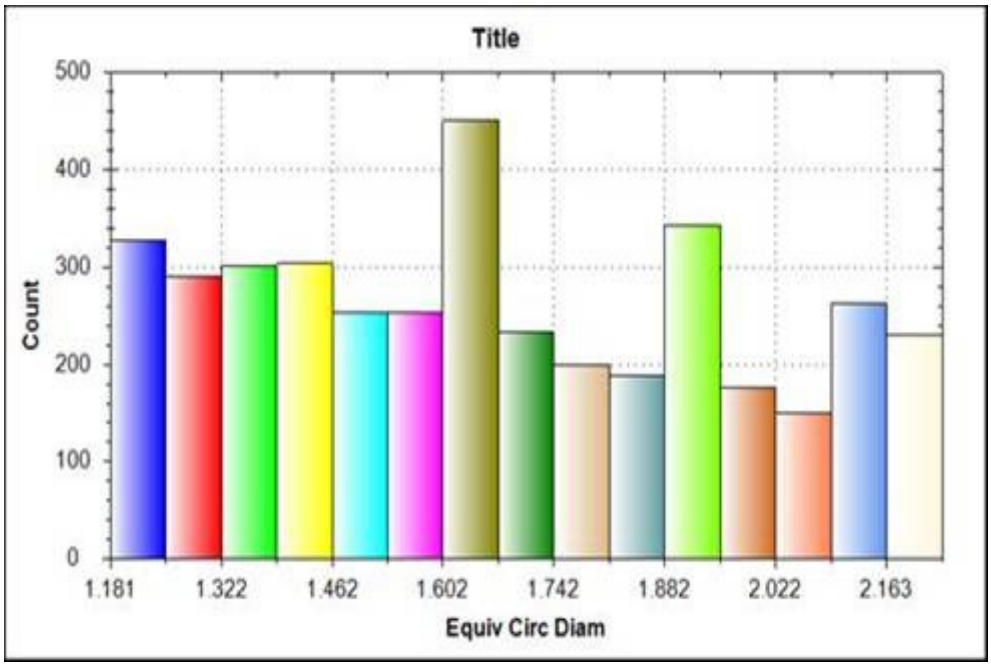


Figure 5-10: **Particle size (µm) distribution obtained for stripping product from 45 g/l uranium solution**

In conclusion, uranium can be recovered from the ammonium carbonate leaching solutions by heating the solution to strip out ammonia and carbonate dioxide. These gases can be re-absorbed in water to regenerate the lixiviant, or could be sparged directly into the leaching vessel.

During the precipitation process, the pH was found to decrease, with visible precipitation occurring from pH 7.8 onwards. By the time a pH of 6.2 had been reached, about 97% of uranium had been precipitated.

It was shown that the hydrated U(VI) oxide that is obtained by the stripping recovery process is easy filterable when using pregnant solutions with a uranium concentration above 20 g/l.

At lower uranium concentrations the precipitate is very fine, unless a suitable surfactant is added.

6. CONCLUSIONS

This investigation has made possible the determination of leaching kinetics for various leaching conditions of uranium residue in carbonate media.

According to the experimental evidence, the dissolution rate of uranium dioxide fuel pellets increases with temperature within the range of 25-60 ^{o}C, with complete dissolution observed at 40 ^{o}C after 30 minutes of leaching in ammonium carbonate solution. Indeed, the dissolution of uranium (IV) in the residue has yielded the same rate under identical reaction conditions. Thus, the dissolution is highly enhanced by the temperature in the range investigated.

Maximum dissolution rate of uranium from uranium dioxide fuel pellets and uranium residue in ammonium carbonate solution was observed with the addition of 1 M hydrogen peroxide.

However, it was observed that the uranium residue dissolves in carbonate solutions without hydrogen peroxide present, while the rate of uranium dioxide dissolution is null under the same working conditions. As would be expected, the dissolution rate of uranium from uranium dioxide was lower than for the uranium residue when small amounts of hydrogen peroxide were present. The above differences are due to the fact that the residue contains appreciable U(VI) that readily dissolves even in the absence of an oxidant.

The activation energy for the dissolution of uranium contained in the residue found to be 45.5kJ/mol confirms a chemically controlled process for uranium dissolution in ammonium carbonate solution with hydrogen peroxide under the conditions investigated. The order of reaction with respect to uranium concentration was found to be unity.

It was shown that the kinetics of uranium residue dissolution are similar to those of uranium dioxide dissolution in the presence of hydrogen peroxide.

The use of ammonium carbonate rather than sodium carbonate is advantageous in improving the rate of reaction. This appears to be a viscosity effect. A major advantage of this lixiviant is the ability to have a largely closed flowsheet, with attendant environmental benefits.

7. RECOMMENDATIONS FOR FUTURE WORK

The residue used in this study was a non – irradiated simulated sample. To confirm the present results, dissolution studies with ammonium carbonate solution enriched with hydrogen peroxide in a hot cell of uranium residue generated during the production of molybdenum-99 must be investigated.

In addition, the characterization of the uranium speciation in the solid residue will help to establish the dissolution mechanism of the residue.

8. REFERENCES

AIChEMI (1981): *Kinetics.* Serie E. America institute of chemical Engineers.

Clarens, F., de Pablo, J., Casa, I., Gimenez, J., Rovira, M., Merino, J., Cera, E., Bruno, J., Quinones, J., Martinez-Esparza, A. 2005. *The oxidative dissolution of unirradiated UO_2 by hydrogen peroxide as a function of pH. Journal of nuclear materials,* Vol. 345, pages 225-231.

Chuck, Z.S., Amanda, M.J., Bruce, K.M., Brady, D.H., Jeffrey, W.C., Katharine, J.C., and

Peper, S. 2011. *Dissolution of irradiated commercial UO_2 fuels in ammonium carbonate and hydrogen peroxide*. Industrial Engineering Chemistry Research, Vol. 50, pages 1813-1818.

De Pablo, J., Gimenez, J.1999.*The role of pe, pH, and carbonate on the solubility of UO_2 and uraninite under nominally reducing conditions*. Pergamon. Geochimica et Cosmochimica Acta, Vol. 62, No. 13, pages 2233-2231.

Du Preez, J.G.H., Morris, D.C., and Van Vuuren, C.P.J. 1981. *The chemistry of uranium. Part XXVII. Kinetics of the dissolution of uranium dioxide powder in a solution containing sodium carbonate, sodium bicarbonate and potassium cyanide*. Hydrometallurgy, Vol. 6, issues 3-4, pages 197-201.

Dong-Yong, C., Heui-Seung, S., Jae-Won, L., Eil-Hee, L., and Kwang-Wook, K. 2010. *Oxidative leaching of uranium from SIMFUEL using Na_2CO_3-H_2O_2 solution*. Journal of Radioanalytical and Nuclear Chemistry, Vol. 284, pages 123-129.

Grandstaff, D.E. 1976. *A kinetic study of the dissolution of uraninite*. Economic Geology, Vol. 71, pages 1493-1506.

Grenthe, I., Fuger, J., Konings, R.J.M., and Wanner, H. 1992. *Chemical thermodynamics of uranium.* Thermochemical Database Project Publications, Vol. 1, pages 318-328.

Hayes, P., 2003. *Process Principles in Minerals and Materials Production.* Hayes Publishing Co. Third edition, pages 592-593.

Hardy, J.C. 2008. *Mining, milling, conversion and enrichment of uranium ores.* Short course. Vanderbilt university. USA

International Critical Tables. Vol V, 1st Edition, 1929, Mc Graw-Hill

Kinnaird, J.A. and Nex, P. *Assessing the geological occurrences of uranium in Africa. Implication for mining and processing.* Uranium Mining and Exploration Conference. Johannesburg 2008, South Africa.

Levenspiel, O. 1999. *Chemical reaction engineering*. 3rd Ed. John Wiley & Sons, pages 38-75.

Merrit, R.C.1971. *The extractive metallurgy of uranium.* Colorado School of Mines of Research Institute, USA. Pages 85-86.

Naidoo, J. and Zeevaart, J.R. 2005. *Report on further experimental investigations into the possibilities for uranium recovery.* Necsa internal report. RC.VLG-0099.

Nowak, P. 1989. *The kinetics of chemical decomposition of ammonium bicarbonate and carbonate in aqueous solutions*. Chem. Eng. Sc, Vol. 44, No. 10, pages 2375-2377.

Pearson, R.L., and Wadsworth, M.E. 1958. *A kinetic study of the dissolution of UO_2 in carbonate solution.* Trans. Met. Soc. AIMS. Vol. 212, pages 294-300.

Peper, S.M., Brodnax, L.F., Field, S.E., Zehnder, R.A., Valdez, S.N., and Runde, W.H. 2004. *Kinetic study of the oxidative dissolution of UO_2 in aqueous carbonate media.* Industrial and Engineering Chemistry Research, Vol. 43, pages 8188-8193.

Pierce, E.M., Icenhower, J.P, Serne, R.J., and Catalano, J.G. 2005. *Experimental determination of UO_2 (cr) dissolution kinetics: Effects of solution saturation state and pH.* J. Nuc. Mat. Vol. 345, pages 206-218.

Pinkney, E.T., Lurie, W. and Van Zyl, P.C.N. 1962. *Chemical processing of uranium ores.* International Atomic Energy Agency-Vienna. Review Series No. 23/24, pages 17-21.

Robert, C.W., and Melvin, J.A. 1981. *CRC Handbook of Chemistry and Physics*. CRC Press, Inc. B-75.

Schortmann, W.E., and DeSeSa, M.A. 1958. *Kinetics of the dissolution of uranium dioxide in carbonate-bicarbonate solutions.* Proceedings of the Second United Nations International Conference on the Peaceful uses of Atomic Energy. Geneva. Vol. 3, pages 333-341.

Sharma, j. N., Battacharya, K., Swami, R.G., Tangri,S.K., Mukherjee,T.K. 1996. *Study on the kinetics of UO_2 dissolution in carbonate-bicarbonate medium using sodium hypochlorite as oxidant*. Elsevier. J. R. N. Letters 214(3), pages 223-233.

Smith, S.C., Peper, S.M., Douglas, M., Kate, L.Z., Finn, E.C. 2009. *Dissolution of uranium under alkaline oxidizing conditions.* J. Radioanal Nucl Chem. Vol. 282, pages 617-621

Stepanov, S.I., Boyarintsev, A.V., Vazhenleov, M.V., Myasoedov, B.F., Nazarov, E.O., Safiulina, A.M., Tananaev, I.G., Hen Vin So., Chekmarev, A.M. and Civadze, A.Yu. 2011. *Carbex process: A new technology of reprocessing spent nuclear fuel.* Russian journal of general chemistry, Vol. 81, No. 9, pages 1949-1959.

Torrero, M.E., Baraj, E., de Pablo, J., Duro, L., Casas, I., and Bruno, J. 1998. *Oxidative dissolution mechanism of uranium dioxide at 25^oC*. Goldschmidt conference, Toulouse, France.

9. APPENDICES

APPENDIX 1: Results of UO_2 dissolution

Table 1: % UO_2 Dissolved in 1M $(NH_4)_2CO_3$ with 0.1M H_2O_2 and variables solid-liquid ratio (**S/L**) at 25° C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	18.6	22.6	24
30	27.3	30	33.2
45	40.1	43.8	48.7
60	57.6	60.1	63.8

Table 2: % UO_2 Dissolved in 1M $(NH_4)_2CO_3$ with 0.5M H_2O_2 and variables solid-liquid ratio (**S/L**) at 25° C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	20.1	23.4	22.1
30	28.9	33.1	35.6
45	45.3	49.5	50.1
60	63	68.6	67.2

Table 3: % UO_2 Dissolved in 1 M $(NH_4)_2CO_3$ with 1 M H_2O_2 and variables solid-liquid ratio (**S/L**) at 25° C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	28.8	32.1	32.8
30	40.9	45.8	47.2
45	57.4	57.9	54.1
60	71.6	76.1	74.2

Table 4: % UO_2 Dissolved in 1M $(NH_4)_2CO_3$ with 0.1M H_2O_2 and variables solid-liquid ratio (**S/L**) at 40° C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	30.6	33.6	34
30	41.4	50.1	52.1
45	58.8	68.1	65.4
60	69	73	80.6

Table 5: % UO_2 Dissolved in 1M $(NH_4)_2CO_3$ with 0.5 M H_2O_2 and variables solid-liquid ratio (**S/L**) at 40^o C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	36.7	36.5	36.1
30	47.5	54.9	60.3
45	67.7	80.5	79.2
60	76.2	85.7	88.2

Table 6: % UO_2 Dissolved in 1 M $(NH_4)_2CO_3$ with 1 M H_2O_2 and variables solid-liquid ratio (**S/L**) at 40^o C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	46.9	50.8	49.6
30	67.4	67.1	69
45	90.9	85.5	94.5
60	97.5	98.4	98.1

Table 7: % UO_2 Dissolved in 1 M $(NH_4)_2CO_3$ with 0.1 M H_2O_2 and variables solid-liquid ratio (**S/L**) at 50^o C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	37.6	47.1	55.6
30	48.3	54.7	64.3
45	67.6	69.1	76.6
60	72.4	76.4	82.1

Table 8: % UO_2 Dissolved in 1 M $(NH_4)_2CO_3$ with 0.5 M H_2O_2 and variables solid-liquid ratio (**S/L**) at 50 ^{o}C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	49.9	53	57
30	57.8	66.5	70.6
45	71.4	83	81.4
60	79.5	89.4	90.9

Table 9: % UO_2 Dissolved in 1 M $(NH_4)_2CO_3$ with 1 M H_2O_2 and variables solid-liquid ratio (**S/L**) at 50 ^{o}C

Time in Min	S/L: 1/40	S/L: 1/60	S/L: 1/80
15	54.1	63.8	61
30	70.9	73	71.8
45	92.2	91.4	96.2
60	99.1	99.3	98.7

APPENDIX 2: Reproducibility tests and other data

Table 10: Effect of peroxide concentration on uranium dioxide dissolution at 25 °C; S/L: 1/60

	15 Min			30 Min			45 Min			60 Min		
$[H_2O_2]$	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**
1st Trial	22.6	23.4	32.1	30	33.1	45.8	43.8	49.5	57.9	60.1	68.6	76.1
2nd Trial	21.3	25.1	33.1	28.4	32.6	44.6	45.1	47.4	54.2	58.7	70.6	77.3
MEAN	21.9	24.2	32.6	29.2	32.8	45.2	44.4	48.4	56.0	59.4	69.6	76.7
STDEV	0.9	1.2	1.1	1.1	0.35	0.8	0.9	1.4	2.6	0.9	1.4	0.8
SQRT(n)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
ST ERR	0.6	0.8	0.5	0.8	0.25	0.6	0.6	1.0	1.8	0.7	1	0.6

Table 11: Effect of peroxide concentration on uranium dioxide dissolution at 40 °C; S/L: 1/60

	15 Min			30 Min			45 Min			60 Min		
$[H_2O_2]$	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**
1st Trial	33.6	36.5	50.8	50.1	54.9	67.1	68.1	80.5	85.5	73	85.7	98.4
2nd Trial	33.1	37.1	48.7	52.1	56.0	68.3	69.0	82.0	86.1	72.0	84.1	98.6
MEAN	33.3	36.8	49.7	51.1	55.4	67.1	68.5	81.2	85.8	72.5	84.9	98.5
STDEV	0.3	0.42	1.4	1.41	0.77	0.8	0.6	1.1	0.4	0.7	1.1	0.1
SQRT(n)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
ST ERR	0.2	0.3	1.0	1	0.5	0.6	0.4	0.7	0.3	0.5	0.8	0.1

Table 12: Effect of peroxide concentration on uranium dioxide dissolution at 50 ^{o}C; S/L: 1/60

	15 Min			30 Min			45 Min			60 Min		
[H_2O_2]	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**
1st Trial	47.1	53	63.8	54.7	66.5	73.0	69.1	83.0	91.4	76.4	89.4	99.3
2nd Trial	49.2	54.1	63.1	56.1	68.0	73.4	70.9	82.9	90.0	75.8	90.0	99.1
MEAN	48.1	53.5	63.4	55.4	67.2	73.2	70.0	82.9	90.7	76.1	89.7	99.2
STDEV	1.4	0.7	0.4	0.9	1.1	0.3	1.3	0.1	0.9	0.4	0.4	0.1
SQRT(n)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
ST ERR	1.0	0.5	0.3	0.7	0.7	0.2	0.9	0.05	0.7	0.3	0.3	0.1

Table 13: Effect of various temperatures on uranium dioxide dissolution; S/L: 1/60

	15 Min			30 Min			45 Min			60 Min		
Temperature	**25^{o} C**	**40^{o} C**	**50^{o} C**	**25^{o} C**	**40^{o} C**	**50^{o} C**	**25^{o} C**	**40^{o} C**	**50^{o} C**	**25^{o} C**	**40^{o} C**	**50^{o} C**
1st Trial	32.1	50.8	63.8	45.8	67.1	79.8	57.9	85.5	91.4	99.3	76.1	99.5
2nd Trial	32.8	49.6	63.0	47.2	69.0	70.6	54.1	88.7	93.4	98.1	74.2	99.4
MEAN	32.4	50.2	63.4	46.5	68.1	75.2	56.0	87.1	92.2	98.7	75.1	99.4
STDEV	0.5	0.8	0.6	0.9	1.3	6.5	2.7	2.3	1.2	0.8	1.3	0.07
SQRT(n)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
ST ERR	0.3	0.6	0.4	0.7	0.9	4.6	1.9	1.6	0.9	0.6	0.9	0.05

Table 14: Dissolution of uranium dioxide in an Autoclave

Temperature	**25° C**	**40° C**	**50° C**	**60° C**	**80° C**
1st Trial	77.3	98.6	99.1	98.2	61
2nd Trial	78.6	99.0	99.4	98.1	84.6
MEAN	77.9	98.8	99.2	98.5	72.8
STDEV	0.9	0.2	0.2	0.6	16.6
SQRT(n)	1.4	1.4	1.4	1.4	1.4
ST ERR	0.6	0.2	0.1	0.4	11.8

Table 15: Effect of solid-liquid ratio

Time in Min	**S/L: 1/40**	**S/L: 1/60**	**S/L: 1/80**
15	56	65	64.9
30	72.9	72.4	70.8
45	91.6	93.2	97.4
60	98.1	99.1	99.3

Table 16: Effect of hydrogen peroxide concentration on uranium residue dissolution at pH 9

[H_2O_2] in M	**1 Hour**	**2 Hours**	**3 Hours**	**4 Hours**
0	71.1	72.2	77.5	83.1
0.1	77.3	84.4	85.4	90
0.5	80.6	88	89.3	95.6
1	90	92.4	96.1	97.8

Table 17: Effect of hydrogen peroxide concentration on uranium residue dissolution at pH 10

Time in Hours	0M [H_2O_2]	0.1M [H_2O_2]	0.5M [H_2O_2]	1M [H_2O_2]
1	60.6	75.1	87.3	88.6
2	71	86.4	88.2	91
3	74.1	89.8	88.4	86.9
4	82	91.4	87	94.8

Table 18: Effect of Na_2CO_3 and $(NH_4)_2CO_3$ on uranium residue dissolution

	1 Hour	2 Hours	3 Hours
1M Na2CO3	79	81.9	83
0.5M Na2CO3	82	83	86.4
1M (NH4)2CO3	84.6	96.8	98

Table 19: Effect of [H_2O_2] on uranium residue dissolution

	1 Hour	2 Hours	3 Hours	4 hours
0.5M Na2CO3	90	93.8	96	97.4
1M Na2CO3	88.4	90.6	88	95
1M (NH4)2CO3	98.6	99.1	99.4	99.7

Table 20: Effect of [H_2O_2] on uranium residue dissolution in $(NH_4)_2CO_3$ solution

Time in Hours	0.1M	0.5M	1M
0	0	0	0
0.5	60.1	74	99
1	80.4	96.7	99.4
1.5	83	95.4	99.3
4	85.8	98.1	99.6

APPENDIX 3: Uranium dioxide leach kinetics

Table 21: Kinetics data for uranium dioxide dissolution in 1 M ammonium carbonate with 0.1M hydrogen peroxide

T (^{o}C)	T(K)	1/T(K)	ln k	k(s^{-})
25	298	3.35E-03	-8.29	0.00025
40	313	3.19E-03	-7.93	0.00036
50	323	3.10E-03	-7.79	0.00041

Table 22: Kinetics data for uranium dioxide dissolution in 1M ammonium carbonate with 0.5M hydrogen peroxide

T (^{o}C)	T(K)	1/T(K)	ln k	k(s^{-})
25	298	3.35E-03	-8.02	0.00033
40	313	3.19E-03	-7.52	0.00054
50	323	3.10E-03	-7.4	0.00061

Table 23: Kinetics data for uranium dioxide dissolution in 1M ammonium carbonate and 1 M hydrogen peroxide solution

T (^{o}C)	T(K)	1/T(K)	ln k	k(s^{-})
25	298	3.35E-03	-7.85	0.00039
40	313	3.19E-03	-6.78	0.00114
50	323	3.10E-03	-6.57	0.0014

Table 24: Data for first, second and zero order plot at 25 ^{o}C

Time in sec	1/[UO2]	ln [UO2]	[UO2]
0	16.13	-2.78	0.062
900	23.8	-3.17	0.042
1800	30.3	-3.41	0.033
2700	38.46	-3.65	0.026
3600	66.67	-4.19	0.015

Table 25: Data for first, second and zero order plot at 40 ^{o}C

Time in sec	1/[UO2]	ln[UO2]	[UO2]
0	16.13	-2.78	0.062
900	33.33	-3.51	0.03
1800	50	-3.91	0.02
2700	111.11	-4.71	0.009
3600	1000	-6.91	0.001

Table 26: Data for first, second and zero order at 50 ^{o}C

Time in sec	1/[UO2]	ln [UO2]	[UO2]
0	16.13	-2.78	0.062
900	45.45	-3.82	0.022
1800	58.82	-4.07	0.017
2700	200	-5.29	0.005
3600	2500	-7.82	0.0004

Table 27: Data for reaction order with respect to H_2O_2 and $(NH_4)_2CO_3$ at 25 ^{o}C

Time in sec	ln[H_2O_2]	ln[$(NH_4)_2CO_3$
0	0	0
900	-0.02	-0.062
1800	-0.03	-0.091
2700	-0.036	-0.114
3600	-0.048	-0.15

Table 28: Data for reaction order with respect to H_2O_2 and $(NH_4)_2CO_3$ at 50 ^{o}C

Time in sec	ln[H_2O_2]	ln[$(NH_4)_2CO_3$
0	0	0
900	-0.04	-0.13
1800	-0.046	-0.14
2700	-0.059	-0.19
3600	-0.064	-0.2

APPENDIX 4: Uranium residue leach kinetics

Table 29: Data for first, second and zero order at 25 °C

Time in sec	1/[UO_2]	ln [UO_2]	[UO_2]
0	16.13	-2.78	0.062
1800	23.8	-3.17	0.042
3600	55.5	-4.02	0.018
5400	62.5	-4.13	0.016

Table 30: Data for first, second and zero order at 50 °C

Time in sec	1/[UO_2]	ln [UO_2]	[UO_2]
0	16.13	-2.78	0.062
1800	28.57	-3.35	0.035
3600	2500	-7.82	0.0004
5400	2703	-7.9	0.00037

Table 31: Data for first, second and zero order at 60 °C

Time in sec	1/[UO_2]	ln [UO_2]	[UO_2]
0	16.13	-2.78	0.062
1800	1470	-7.29	0.00068
3600	2041	-7.62	0.00049
5400	3226	-8.07	0.00031

Table 32: Data for reaction order with respect to H_2O_2 and $(NH_4)_2CO_3$ at 25 °C

Time in sec	ln[H_2O_2]	ln[$(NH_4)_2CO_3$
0	0	0
1800	-0.02	-0.062
3600	-0.045	-0.14
5400	-0.047	-0.15

Table 33: Data for reaction order with respect to H_2O_2 and $(NH_4)_2CO_3$ at 50 °C

Time in sec	ln[H_2O_2]	ln[$(NH_4)_2CO_3$
0	0	0
1800	-0.027	-0.084
3600	-0.06	-0.2
5400	-0.064	-0.2

APPENDIX 5: Determination of U with the H_2O_2/CO_3^{2-} method

I. Preparation of a calibration curve

1. Prepare four standard solutions using a 1000 ppm absolute U standard solution: Into four 25 ml volumetric flasks, pipette respectively 1.25; 2.5; 3.75 and 5 ml of the standard solution

2. Add 3 ml Na_2CO_3 2M to each flask

3. Add 1 ml H_2O_2 30% to each flask

4. Dilute to 25 ml with water, and mix

5. Prepare a reagent blank by diluting 3 ml Na_2CO_3 2M and 1 ml H_2O_2 30% to 25 ml

6. Change the wavelength to 450 nm

7. Fill the two 1 cm cuvettes with blank solution and place a cuvette in each of the reference (at the back) and sample (at the front) beams. Close the cover

8. Change the absorbance value shown on display to zero

9. Empty the cuvette placed in the sample and fill with one of the standard solution. Write down the absorbance value displayed

10. Repeat 9 above for all the standards

11. Obtain a calibration curve by plotting the absorbance values vs. the U concentration of the standards

II. Determination of samples

1. From the approximate expected value of U concentration of a sample, calculate the amount of solution which would give a U concentration in the range of the above calibration curve, when diluted to 25 ml. pipette this volume into a 25 ml volumetric flask

2. Repeat steps 2 to 10 above for all the samples

3. Using the equation for the calibration curve, calculate the U concentration of the sample

APPENDIX 6: Determination of U with the Bromo-Padap method

I. Preparation of a calibration curve

1. Prepare four standard solutions using a 25 ppm absolute U standard solution: Into four 25 ml volumetric flasks, pipette respectively 0.5; 1; 1.5 and 2 ml of the standard solution

2. Add 2 ml CDTA complexing solution to each flask

3. Add 2 ml TEA buffer solution to each flask

4. Add 10 ml ethanol to each flask

5. Add 2 ml Bromo-Padap solution to each flask

6. Dilute to 25 ml with water, and mix

7. Prepare a reagent blank by diluting 2 ml CDTA, 2 ml TEA Buffer, 10 ml ethanol and 2 ml Bromo-Padap solution to 25 ml

8. The absorbance of these standards must be measured on the Carey spectrophotometer only after a period of 40 minutes, when optimal colour development has been reached

9. Change the wavelength to 578 nm

10. Fill the two 1 cm cuvettes with blank solution and place a cuvette in each of the reference (at the back) and sample (at the front) beams. Close the cover

11. Empty the cuvette placed in the sample beam, and fill with one of the standard solutions. Write down the absorbance value displayed

12. Repat 11 above for all the standards

13. Obtain a calibration curve by plotting the absorbance values vs. the U concentration of the standards

II. Determination of samples

1. From the approximate expected value of U concentration of a sample, calculate the amount of the solution which will give a U concentration in the range of the calibration, when diluted to 25 ml. pipette this volume into a 25 ml volumetric flask

2. Repeat steps 2 to 12 above for the samples. Samples which are acidic, should first be neutralised to pH 8 with 1M NaOH, before adding of reagents

3. Using the equation for the calibration curve, calculate the U concentration of the sample.