

# Influence of Physico-chemical Conditions on Mobility of Uranium from Wastes

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**Abstract:** Dynamic leaching tests were carried out on solid wastes generated from the uranium mining and milling industry under different physico-chemical conditions to assess the mobility of uranium from these matrices. The mobile/ soluble fraction of uranium leached out very slowly; being faster in the initial stages and then attaining a near steady state condition in most cases. Uranium leaching was observed to increase with decreasing initial pH, reducing particle size and increasing temperatures. A maximum of 2.4% uranium was leached out under highly acidic conditions in the experimental time period. Leachability index values indicated weak leaching of uranium from the wastes under all conditions. Leaching kinetics was examined with the help of a heterogeneous reaction model. Model results and apparent activation energy values indicated the leaching process to be initially reaction controlled and subsequently diffusion controlled. The apparent rate constants displayed dependence on the particle sizes of the tailings. All results obtained from this study imply that the extent of uranium leaching from these solid mining wastes is extremely low. This indicates low mobility and negligible transfer to other environmental compartments.

**Keywords:** Uranium; Mining wastes; Mobility; Batch leaching; Leachability index; Kinetics

**1. Introduction:** Uranium is the basic fuel of the present global nuclear power programme. This radiologically and chemically toxic element has been prevalent in the atmosphere, hydrosphere, lithosphere and biosphere with wide variation in concentration since the inception of the Earth [1]. It is present in ppm levels in soils to a few percentages in minerals/ rocks used in the mining industry and also in the waste forms generated. The presence of uranium in surface water, groundwater and seawater arises due to its mobility from soil/sediment/rock into the water medium depending on several factors like, the initial U concentration in the solid matrix, pH of the system, redox potential, concentration of complexing anions, concentration of competing ions, porosity of the medium, ambient temperature, presence of organic compounds, amount of water available for leaching, flow rate of water and microbial activity [2].

The potentially harmful constituents from any mineral/rock/waste used in the mining industry may contaminate the groundwater by geological processes like leaching and erosion, as runoff and waters percolating through these materials carry the constituents eventually into the aquifers or surface streams. Many leaching procedures have been developed with the aim of assessing the risk associated with such solid matrices [3]. These leaching procedures are useful tools to assess the impact of changing conditions on long-term release of pollutants from a matrix to evaluate their potential environmental impact. Apart from mathematical modeling, leaching tests also estimate the elemental release under field management scenarios [4]. Because the leaching process is inherently extremely complex, no single leaching test or a set of leaching conditions is appropriate for a wide variety of objectives and

applications [5]. Equilibrium leaching tests offer more realistic simulation of long-term leaching processes that occur in environmental conditions [6]. In such tests the material is in contact with the leaching solution and the variables generally include: contact time, agitation rate, pH of the leachate solution and L/S ratio [5]. Equilibrium batch leaching tests offer the advantage of simple design, high reproducibility and shorter experimental period, ranging from a few hours to a few days. For the above advantages, and in order to provide a better tool for decision-making, the equilibrium batch tests have been used routinely to study the environmental fate and transport of pollutants. Dynamic leaching tests include multiple or serial batch test, and percolation and flow through (i.e., column) tests [7].

The mining of uranium bearing minerals is essential for the extraction of uranium to meet the power requirements of India [8]. Mining and milling activities produce large quantities of low active tailings that are contained in engineered Tailings Ponds. The nature of tailings depends on the mineralogy of ore and host rock and their quantity depends on the configuration of the ore body and mining methods [9]. Mine tailings are generally characterized by low pH, low organic carbon content and high levels of heavy metals. These tailings are amenable for interaction with the geochemical forces of leaching and infiltration and hence can act as a potential source of contamination [10]. This necessitates the physical and chemical characterization of the tailings as well as studying the mobility of contaminants therefrom under different simulated environmental conditions. The mobility of the contaminants may lead to their presence in the groundwater, leading to their eventual uptake by plants which ultimately culminate in the human food chain.

Mining and processing of low-grade uranium ore commenced in the mid-sixties and has since been carried out at different locations in the Singhbhum Thrust Belt (STB) of Eastern India

[11]. The low grade ore from these mines is processed at the ore processing plant at Jaduguda. A hydrocyclone separates the finer fraction of the solid tailings ( $<74 \mu\text{m}$ ) from the coarser fraction. A final alkaline pH is maintained in the solid tailings, which are then pumped to engineered tailings ponds for permanent containment [12]. The solid mass settles down and the clear liquid is decanted and sent to the Effluent Treatment Plant. At Jaduguda, around  $1.5 \times 10^5$  tonnes per annum of tailings are disposed in the Tailings Ponds [13,14].

In the present study, equilibrium batch leaching has been employed to represent the mobility of uranium from mill tailings generated from the uranium mining industry and its release has been studied over widely varying physicochemical conditions (e.g., contact time, particle size of sample, pH of leachate solution, temperature etc.). LED fluorimetry has been used as the analytical tool to quantify the amount of uranium extracted into the leachate solution. The amounts of uranium leached out under different conditions, cumulative leach fraction (CLF) and leaching intensities have been calculated. The kinetics of uranium leaching has also been modeled using a heterogeneous reaction model. Hence this study gives an insight into the influence of different physicochemical conditions on uranium leaching from mining wastes and the governing kinetic processes.

**2. Physiography of the region:** Samples were collected from the STB, which is a uranium mineralized region located in Jharkhand State of Eastern India. This hilly and undulating terrain, falling within the Singhbhum Shear Zone, is known for hosting vein/disseminated type of uranium deposits [15]. The uranium mineralisation has occurred primarily within the narrow cracks in Arachean metamorphic rocks, filled with pitchblende as the primary mineral, and are hence named vein type deposits [16]. This region receives an annual rainfall of around 1200 mm and experiences true tropical climate.

Maximum temperature of 39-42°C is observed during the summer months (March to May) and average temperature in the winter months (November to February) comes down to 9-15 °C. Relative humidity ranges from nearly 50% in the summer to 85% in the monsoons (June to September) [17].

### 3. Materials and Methods

#### 3.1. Sample collection and processing:

Uranium bearing tailings were collected from the tailings ponds located in the study area. Tailings samples were collected from the surface of the tailings ponds using random sampling method. Multiple samples were collected from a location and homogenized to make one representative sample by coning and quartering technique [18]. The samples were dried at 80°C till constant weight and then sieved below 2 mm mesh size for use in subsequent experiments. All samples were stored in preconditioned polyethylene containers for further experiments.

**3.2. Physicochemical characterization:** The physicochemical characteristics of samples help us in understanding the association, transport and biological activity of elements present therein. The physicochemical characteristics of the mine tailings were measured following standard methods [19]. In the present study, the pH of the samples was determined by a digital pH meter (Mettler Toledo) at 1:2.5 w/v of soil: ultrapure water. Organic matter content was determined by loss-on-ignition method [20] involving weight loss after calcination of the samples in a muffle furnace at a temperature of 550°C until constant weight was achieved. The samples were separated into different particle size classes by dry sieving using an electromagnetic sieve shaker and by sedimentation method using Stoke's law for the settling velocity of spherical particles. All the measurements were carried out at room temperature (25 °C), wherever applicable [21].

The mean bulk density, pH, porosity and organic matter content of the uranium tailings were  $1.7 \pm$

$0.4 \text{ g/cm}^3$ ,  $6.5 \pm 0.1$ ,  $41 \pm 4.3 \%$  and  $0.9 \pm 0.2 \%$  LOI (Loss on ignition), respectively. The texture of the uranium tailings was observed to be sandy loam, with the sand %, silt % and clay % ranging from 70-80 %, 13-24 % and 2-7 %, respectively. The tailings samples were segregated in different particle size classes and the particle size distribution of a typical tailings sample is given in Figure S1 of supplementary information. The maximum mass fraction for uranium tailings was present in the 63-125  $\mu\text{m}$  particle size class.

**3.3. Elemental analysis:** Major elements and uranium were measured in the samples by CHNS Elemental Analyser (Vario EL Cube), Instrumental Neutron Activation Analysis (INAA) technique and Gamma spectrometric technique.

The CHNS Elemental Analyser works on the principle of combustion of the samples (conversion to gaseous products), subsequent separation of gases in Gas Chromatographic columns and determination of C, H, N and S by a Thermal Conductivity Detector [22].

To perform analysis by relative method of INAA, samples were sealed with Certified Reference Materials and blanks for irradiation. Irradiation was carried out at a neutron flux of  $10^{12}$  neutrons/cm<sup>2</sup>/s and subsequent counting was carried out on a 50 % relative efficiency HPGe detector coupled to a PC based MCA. Details of the procedure are given elsewhere [23]. Prior to gamma spectrometry counting, the samples were dried, homogenized and sealed in standard geometry for 1 month. An n-type vertical germanium detector (DSG, Germany) having 100 % relative efficiency (with respect to 7.6 cm\* 7.6 cm NaI(Tl) detector at 1332 keV of <sup>60</sup>Co gamma energy measured at 25 cm) and associated electronics coupled with 8 K MCA were used for counting. PHAST software (Electronics Division, BARC) was used for spectrum analysis. The detector was surrounded by 7.5 cm thick lead shield. Energy and efficiency calibration of the detector was done

using IAEA Certified Reference Materials (CRMs), RGU-I and RGTh-I. Details of the procedure are given elsewhere [23]. The total concentrations of major elements and uranium in the samples, obtained by the above-mentioned techniques, are given in Table 1.

**Table 1. Major element and uranium concentrations in uranium tailings samples**

Element	Unit	Concentration
Na	%	$0.6 \pm 0.2$
K	%	$0.8 \pm 0.3$
Fe	%	$7.2 \pm 1.3$
C	%	$1.0 \pm 0.8$
H	%	$0.7 \pm 0.3$
N	%	$0.1 \pm 0.03$
S	%	$0.2 \pm 0.1$
U	ppm	$91.2 \pm 5.8$

### 3.4. Dynamic Leaching experiments:

**Physicochemical conditions of leaching:** The goal of equilibrium batch testing was to represent constituent solubility and release of uranium over a range of conditions by varying a physical parameter/condition of leaching (e.g., pH, particle size etc.). The dynamic leaching method involved shaking a known mass of soil (a few grams) with an extractant (ultrapure water) for a predefined period of time on a horizontal shaker at a speed of 80-100 rpm. All experiments were conducted at ambient temperature (22-25 °C), except where the temperature was the variable parameter to study the effect on leaching. A solid: liquid ratio of 1: 25 has been proposed for nutrient leaching; 1:10 for radionuclides and 1:8 for heavy metals [24,25]. If the solid: liquid ratio is kept very low, for example 1:5, there is a possibility of heavy metal re-adsorption onto the solid phase and in such cases the equilibrium condition may not be attained [26]. However, a solid: liquid ratio of 1: 20 was maintained throughout the experiments in this study to minimize any change in leachate

composition and also to ensure adequate concentration of leached uranium for subsequent analysis by LED Fluorimetry. Water was used for these experiments as the leachate, to allow the waste matrix be a dominant factor in determining the pH of the leachate; a scenario similar to the ambient environmental conditions. This is similar to the ASTM test, DIN 38414 S4 batch test of Germany and the AFNOR X 31-210 batch test of France employed for testing elemental leachability from waste matrices [27]. Also, the use of relatively non-specific extractants leads to a kinetic approach towards elemental leachability since measurements of trace elements extracted at equilibrium cannot be related to their speciation. Leachate was separated from the solid matrix by vacuum filtration through 0.22µm membrane filter and analysed for total U concentration by LED Fluorimetry. A portion of leachate was sampled out at regular time intervals and replaced with fresh solvent. All experiments were carried out in duplicate.

The variables during the equilibrium batch tests included: contact time, pH of the leachate solution, temperature during leaching experiment and particle size of the material. Contact time was varied from 2- 95 h for the leaching tests. The samples were subjected to dynamic batch leaching with water as solvent under acidic (pH 4), neutral (pH 7) and basic (pH 9) conditions. Particle sizes of the tailings subjected to dynamic leaching were <36 µm, 36-63 µm, 63-125 µm, 125-212 µm and 212-500 µm. The dynamic leaching tests were carried out under ambient temperature (25 °C) and at an elevated temperature of 40 °C and 60 °C.

**3.5. Analytical technique:** The total uranium content in leachate samples was analysed using a LED based Fluorimeter system fabricated by LED Instruments Section, Raja Ramanna Centre for Advanced Technology, Department of Atomic Energy, India. It is a compact analytical instrument based on fluorimetric technique and micro-optics. The instrument contains a nitrogen

LED (radiation source), sample compartment (sample in quartz cuvette, 9 ml) and a PhotoMultiplier Tube (PMT) placed in right-angle optical configuration. The uranium complex formed in the sample, by the addition of fluorescence enhancing agent, is excited by the LED light, which upon de-excitation emits fluorescence, measured by the PMT. The fluorescence interference originating from organic matters in the samples, is corrected by optical filter, fixed electronic delay and gating. The optical filter at 450 nm and measurement of delayed fluorescence signal helps in nullifying the interference due to organic matter. The working range and Minimum Detection Level (MDL) of the instrument are 0.2-20 µg/L and 0.2 µg/L, respectively.

The leachates generated from the equilibrium dynamic batch tests were analysed by standard addition technique. A working solution (500 µg/L mass concentration) of uranium was used as the standard, for analysis. It was prepared from an Atomic Absorption Standard solution of uranium (973 µg/ml mass concentration, Sigma Aldrich). A typical standard addition curve used for sample analysis is shown in given in Figure S2 of supplementary information.

The concentrations of uranium (ppb) in samples were calculated by using the equation,

$$U \left( \frac{\mu\text{g}}{\text{ml}} \right) = \frac{D_1 * V_1 * C}{(D_2 - D_1) * V_2} \quad (1)$$

Where  $D_1$  is the fluorescence due to sample alone,  $D_2$  is the fluorescence due to sample and U-standard,  $V_1$  is the volume of U-standard added (ml),  $V_2$  is the volume of sample used for analysis (ml) and  $C$  is the concentration of U in U-standard (µg/ml)

**3.6. Quality control:** Appropriate quality-assurance protocols were adopted and precautions were taken to ensure reliability of results. All reagents used in the entire study were of analytical reagent (AR) grade. Ultrapure water (Type-1, ~18.2 MΩ, Barnstead T11, Barnstead Nanopure, Thermo Scientific) was used throughout the study. The laboratory

glassware used for sample processing and storage were soaked in 10% nitric acid for 15d and then rinsed thoroughly with ultrapure water before use. Multiple samples and instrumental/analytical blanks were used throughout the study for quality control purposes. Reagent blank was taken along with each batch of sample during sample processing and the concentrations observed were subtracted from the same batch of samples. Certified reference standards and blanks were analysed for quality control of the measurements. Various precautions were taken in order to achieve a dust-free laboratory environment and steady temperature. Careful handling of the samples was ensured to avoid cross contamination. Statistical quality of the instrumental output was controlled by constructing quality control charts by monitoring the output of the instrument over a long period of time. The various procedures undertaken for quality-control purposes are elaborately mentioned elsewhere [28].

#### 4. Theoretical basis of calculation

**4.1. Cumulative leach fraction:** Uranium leaching was quantified by the cumulative leach fraction (CLF). CLF is a measure of the elemental mobility in terms of the leaching rate, from a sample. It is calculated by the following equation [29]:

$$\text{CLF (cm)} = (\sum A_n / A_0) / \frac{V}{S} \quad (2)$$

where,  $\sum A_n$  is the cumulative content of element leached during the cumulative time  $t_n$ ,  $A_0$  is the initial element content present in the sample,  $V$  is the volume of sample ( $\text{cm}^3$ ), and  $S$  is the exposed surface area of sample ( $\text{cm}^2$ ).

**4.2. Leaching intensity:** Leaching intensity ( $I$ ) is another parameter to quantify elemental leaching.  $I$  for a solid-liquid system can be determined by the following equation [30]:

$$I \text{ (h}^{-1}\text{)} = \frac{[\text{U}] \text{ in leachate } \left(\frac{\mu\text{g}}{\text{ml}}\right) * \text{Volume of Leachate (ml)} * 1000}{[\text{U}] \text{ in sample } \left(\frac{\mu\text{g}}{\text{g}}\right) * \text{Weight of sample (g)} * \text{Time (h)}} \quad (3)$$

The larger the value of I, the greater is the rate of leaching. Wang et al. [30] have classified the elemental leaching from wastes as strong:  $I \geq 5$ ; medium:  $1 \leq I < 5$ ; weak:  $0.5 \leq I < 1$ ; very weak:  $I < 0.5$ .

**4.3. Governing kinetic processes:** It can be considered that chemical reaction in a solid-liquid system is controlled by one or more of the following steps: a) diffusion through the liquid film; b) diffusion through the product layer formed on the surface of the particle; and c) chemical reaction at the surface of unreacted particles which then diffuse across the solid-liquid interface or through the porous solid layer [31]. Considering the dissolution of uranium from mill tailings, if the particles are considered to be spherical, the elemental leaching can be described by the shrinking core model (SCM), a heterogeneous kinetic model. This model considers the dissolution of spherical solid particles in a solid-liquid system [32,33].

For a chemical reaction, the step with the highest resistance is the rate controlling step. According to SCM, if the reaction is controlled by the surface reaction step, the kinetic equation is [34]:

$$1 - (1 - x)^{1/3} = k_r t \quad (4)$$

But, if the reaction rate is controlled by the diffusion step, the kinetic equation is [34]:

$$1 - \frac{2}{3}x - (1 - x)^{2/3} = k_d t \quad (5)$$

where, x refers to the fraction of element reacted/leached, t is the time period of reaction,  $k_r$  and  $k_d$  are the rate constants of chemical reaction step and diffusion step, respectively. These two equations indicate that if the chemical reaction step or the diffusion step is the rate controlling step in the leaching process, then a plot of the left hand side of the equations with

respect to time t will yield a straight line with slopes of  $k_r$  and  $k_d$ , respectively.

The apparent rate constants  $k_r$  and  $k_d$  have been used to study the temperature dependence according to the Arrhenius' equation [34], in Fig. 5:

$$k = A * e^{-E_a/RT} \quad (6)$$

where, A is the frequency factor,  $E_a$  is the activation energy of a chemical reaction, R is the universal gas constant and T is the temperature in K.

**5. Results and Discussion:** Considering the physico-chemical characteristics of the samples, it was observed that porosity and organic matter showed positive correlation with the clay content of these samples, as evident in Table ST1 of supplementary information.

Different physicochemical factors like pH, particle size, time, temperature, concentration of complexing agents, concentration of competing ions, etc. influence the leaching of uranium from a matrix. We have made an effort to investigate the variation of U leaching with the variables like contact time, leachate pH, particle size and temperature from the U tailings, in this study. We have also made an attempt to study the kinetics of uranium leaching from these tailings.

**5.1. Effect of leaching duration:** The leached U concentrations have been observed to increase with time; contact time varying from 2 h to nearly 95 h, considering all experimental conditions. In all the cases, viz. varying pH, temperature and particle size, an initial faster rate of leaching was followed by a slower rate of leaching, which finally reached a near steady state condition in most of the cases. The faster rate of leaching continued nearly for the first 10 h. This trend of leaching can be attributed to biphasic kinetics i.e., a rapid reaction rate

followed by a much slower reaction rate, explained by two first order reactions taking place in the biphasic system [35,36].

**5.2. Effect of leachate pH:** The uranium tailings were subjected to acidic (pH 4), basic (pH 9) and neutral (pH 7) conditions of leaching, with water as the leachate, modified by acid and base, as required. The pH was maintained initially, using small amounts of an acid (dilute nitric acid) and a base (dilute sodium hydroxide). The maximum uranium concentrations were observed in the leachates in the acidic conditions of leaching. The extreme conditions of acidic and alkaline environments do not exist in the natural environment. However, leaching experiments were carried out to assess the extent of increased leaching under these conditions and to ascertain the applicability of the shrinking core model.

In Figure 1(a) it can be seen that the U leached concentrations increased with time under all pH conditions. The uranium leached (%) from the tailings reached a maximum of 19% under acidic pH during the entire leaching time period, as evident from Figure 1(a). The maximum U% leached from the tailings was 0.4% in basic and 0.7% in neutral conditions, respectively. A much

higher rate of U leaching in the acidic conditions may be because of the oxidative dissolution of the pyritic tailings in acidic media [9,37]. Figure 1(b) shows the variation of pH in the leachates with time. It can be observed that the pH in neutral conditions of leaching varies around the neutral pH of 7; leachate pH in this condition is totally dependent on the pH of the sample (uranium tailings). In the basic condition, initially the leachate pH had a dominant role to play, but towards the end the pH of the leachate was dominated by the pH of the sample. For the acidic condition, the pH showed least variation and the leachate pH was dominant throughout the experimental period.

**5.3. Effect of particle size:** The uranium tailings were subjected to dynamic leaching with water for the different particle sizes viz. <36 μm, 36-63 μm, 63-125 μm, 125-212 μm and 212-500 μm. Decrease in the particle size of tailings leads to enhanced U leaching, with the maximum U % leached varying from 0.5 % (212-500 μm) to 2.4 % (< 36 μm). It is evident from Figure 2 that the rate of leaching is higher for smaller particle sizes, which may be due to the increase in surface area with reducing particle size

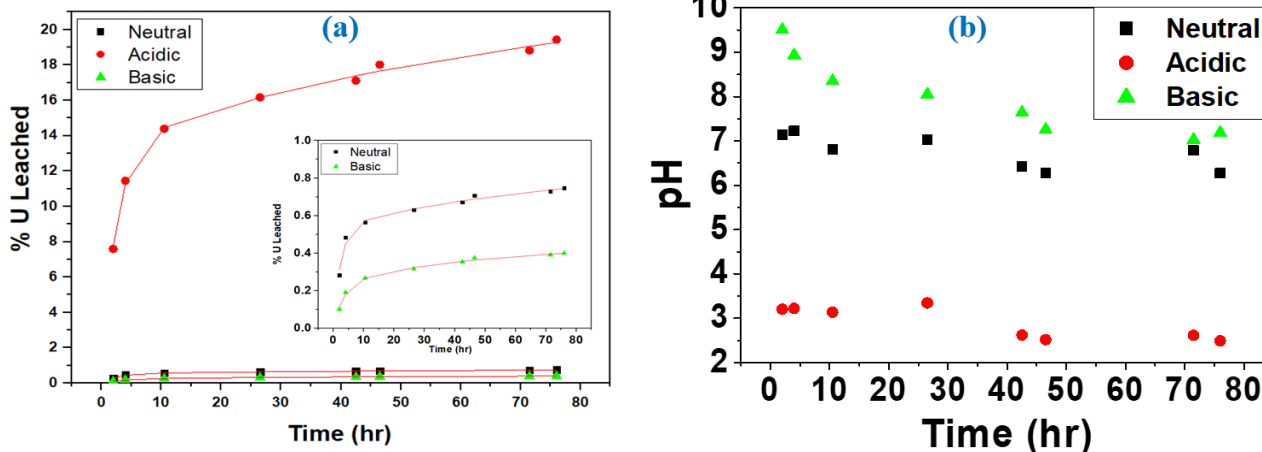


Figure 1. (a) Trend of uranium leaching at different pH; inset showing the zoomed image for neutral and basic pH and (b) variation of pH with time

**5.4. Effect of temperature:** The uranium tailings were subjected to dynamic leaching at 25°C, 40°C and 60°C with water. An increase in uranium% leached was observed with the increase in temperature, reaching a maximum of 0.6% at 25°C and 1% at 60°C, as evident from Figure 3. Again, the rate of uranium leaching was observed to increase at elevated temperatures. The movement of ions increase with an increase in temperature, thus increasing their migration and diffusion, finally resulting in an increase in the rate of chemical reaction.

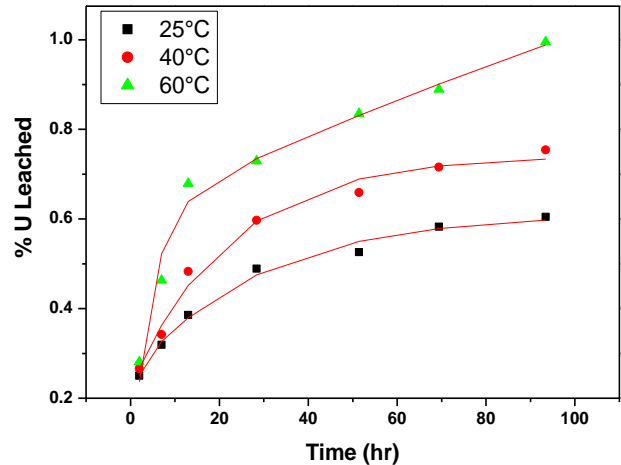


Figure 3. Trend of uranium leaching at different temperatures

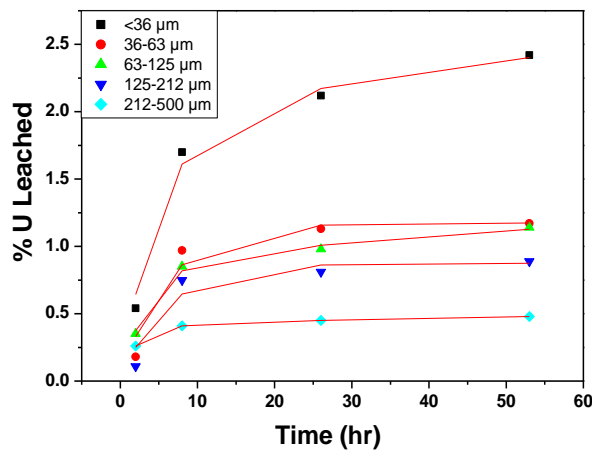


Figure 2. Trend of uranium leaching with different particle sizes

**5.5. Leachability indices:** The U CLF values ranged from 0.001-0.04 cm under the different pH of leaching, as evident from Table 2. The Leaching intensity from the matrices varied from 0.05-2.56 h<sup>-1</sup> in the acidic, basic and neutral conditions of leaching.

**Table 2. Leaching indices under different pH**

Condition	I (h <sup>-1</sup> )	CLF (cm)
Neutral	0.098	0.001
Acidic	2.557	0.039
Basic	0.053	0.001

The leaching indices were higher for the smaller particle sizes compared to the larger ones, as evident from Table 3. The CLF values ranged from 0.001-0.005 cm. The Leaching intensity from the different particle sizes varied from 0.09-0.46 h<sup>-1</sup>.

**Table 3. Leaching indices for different particle sizes**

Particle size	I (h <sup>-1</sup> )	CLF (cm)
<36	0.456	0.005
36-63	0.221	0.002
63-125	0.214	0.002
125-212	0.167	0.002
212-500	0.09	0.001

An increase in the leaching indices was observed with the increase in temperature as evident from Table 4. The CLF values ranged from 0.001-0.002 cm. The Leaching intensity varied from 0.07-0.1 h<sup>-1</sup> from 25- 60°C.

**Table 4. Leaching indices at different temperatures**

Temperature	I (h <sup>-1</sup> )	CLF (cm)
25°C	0.065	0.001
40°C	0.081	0.002
60°C	0.107	0.002

Highest I value was obtained for acidic condition of leaching. Comparing the I values in this study



with literature [30] it can be concluded that the uranium leaching from these wastes ranged from

**5.6. Kinetics of uranium leaching:** The kinetic analysis of uranium leaching from mine tailings was conducted on experimental data obtained from leaching experiments at different temperatures for different time periods. We have made an attempt to divide the uranium leaching process from the tailings into two regions, the initial process being faster and the later process being slower. Considering SCM, we have attempted to fit the experimental data with chemical reaction step in the initial stages of leaching and diffusion step in the later stages, as the rate determining steps. The initial stage has been considered to be upto 13 h from the inception of the leaching time period. The leaching of uranium from the mill tailings at different temperatures for different time periods with respect to the kinetic equations of the SCM are presented in Figure 4. It can be seen from the figure that the experimental data fit the SCM with chemical reaction in the initial stages (<13 h) and diffusion in the late stages.

Usually, high values of  $E_a$  indicate strong influence of temperature on a process as is the case of chemical reaction, whereas low  $E_a$  values indicate weak influence of temperature as in diffusion processes [32]. From Fig. 5 the apparent activation energy of U leaching from tailings in the temperature range of 25-60 °C was calculated to be 25.66 kJ/mol and 14.4 kJ/mol for the chemical reaction and the diffusion step

very weak to weak under all the experimental conditions, except under the acidic condition.

of SCM, respectively. Several authors have used the SCM to calculate the apparent activation energies in elemental leaching from solid wastes [38,39].

Since the activation energy for diffusion process is nearly 20 kJ/mol [40,41], we can conclude from figures 4 and 5 that initially uranium leaching was controlled by surface reaction step being followed by the diffusion step. Also, the apparent activation energy for the chemical reaction control step obtained from this study was considerably low compared to those for typical activation controlled reactions [42].

According to SCM, the constants  $k_r$  and  $k_d$  are related to the particle sizes of the solid in the solid-liquid system. The apparent rate constants from the reaction control step and diffusion step,  $k_r$  and  $k_d$ , vary with the inverse of the particle radius and inverse square of particle radius, respectively [32]. To investigate this relationship we plotted the apparent rate constants with the particle size terms in Figure S3 of supplementary information. It is evident from the figure that  $k_r$  and  $k_d$  have a positive correlation with the particle radii. This further supports the assumption that the uranium leaching in this study follows an initial chemical reaction step followed by a diffusion step, according to the SCM.

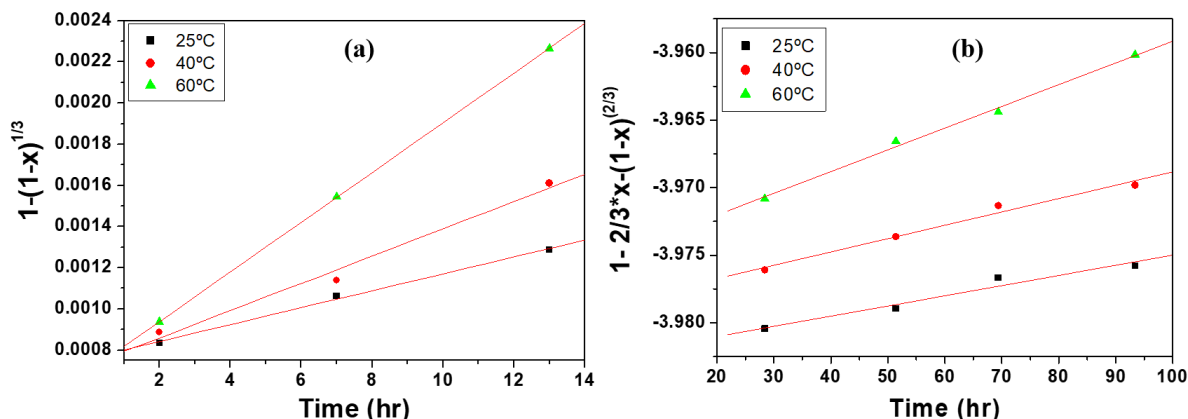


Figure 4. Fits of SCM to experimental data considering, (a) chemical reaction and (b) diffusion through product layer steps (1:20 S/L; Neutral pH; water leachate; 80-100 rpm; composite sample)

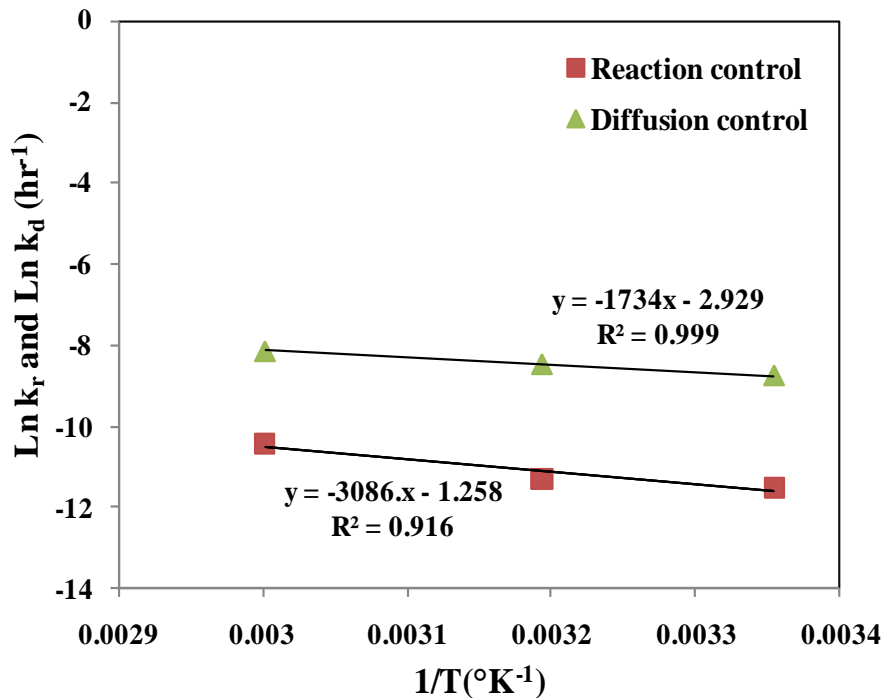


Figure 5. Arrhenius plots of  $k_r$  and  $k_d$  for the experimental data

**6. Conclusions:** The release of uranium from mining wastes was evaluated in this study using a dynamic leaching test using water. The mobile/soluble fraction of uranium leached out under the leaching conditions. Leaching was very slow from all the samples; being faster in the initial stages and then attaining a near steady state condition in most cases.

Leachate pH was observed to be a primary factor for uranium leaching from mining wastes, with the leached uranium content decreasing with increasing pH. Particle size of the tailings was also observed to have an effect on the overall uranium leachability, with smaller particle sizes displaying higher leaching. Uranium leaching also increased with increasing temperatures. Under all experimental conditions the uranium leaching from the tailings were observed to be low, reaching a maximum of 2.4% under acidic pH conditions of leaching. From the values of leaching intensity it can be concluded that uranium leaching from these wastes mostly ranged from very weak to weak. All the results obtained from this study imply that the extent of

uranium leaching from these tailings is extremely low.

The shrinking core model with reaction control and diffusion control fitted the experimental data in the initial stages and final stages of leaching, respectively. The apparent activation energy calculated during the initial stages of leaching was higher than in the final stages; reiterating that the process is chemically controlled during the initial stages and diffusion controlled in the later stages. Also the apparent rate constants displayed dependence on the particle sizes of the tailings, according to the shell core model.

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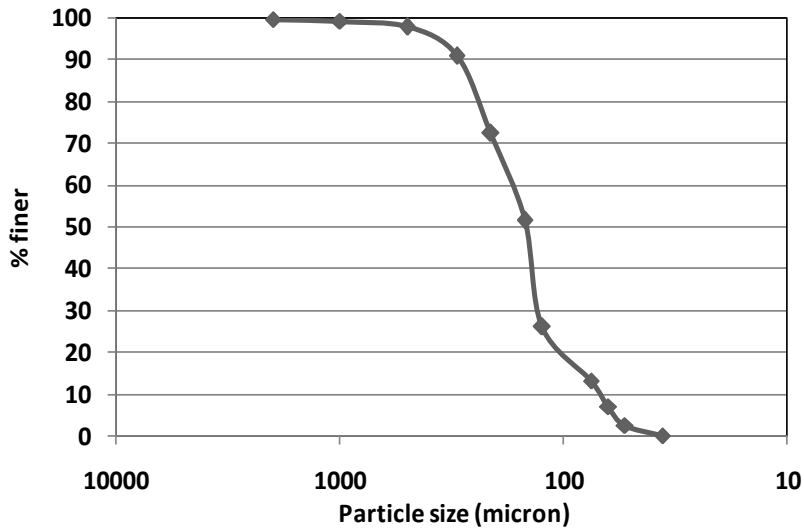
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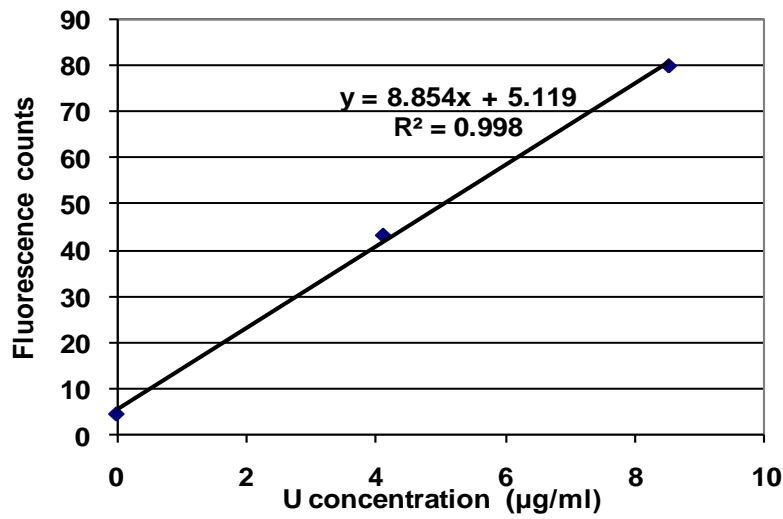
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**Supplementary Information**



**Figure S1. Particle size distribution of uranium tailings**



**Fig S2. Typical standard addition curve for U analysis by Laser Uranium Analyser**

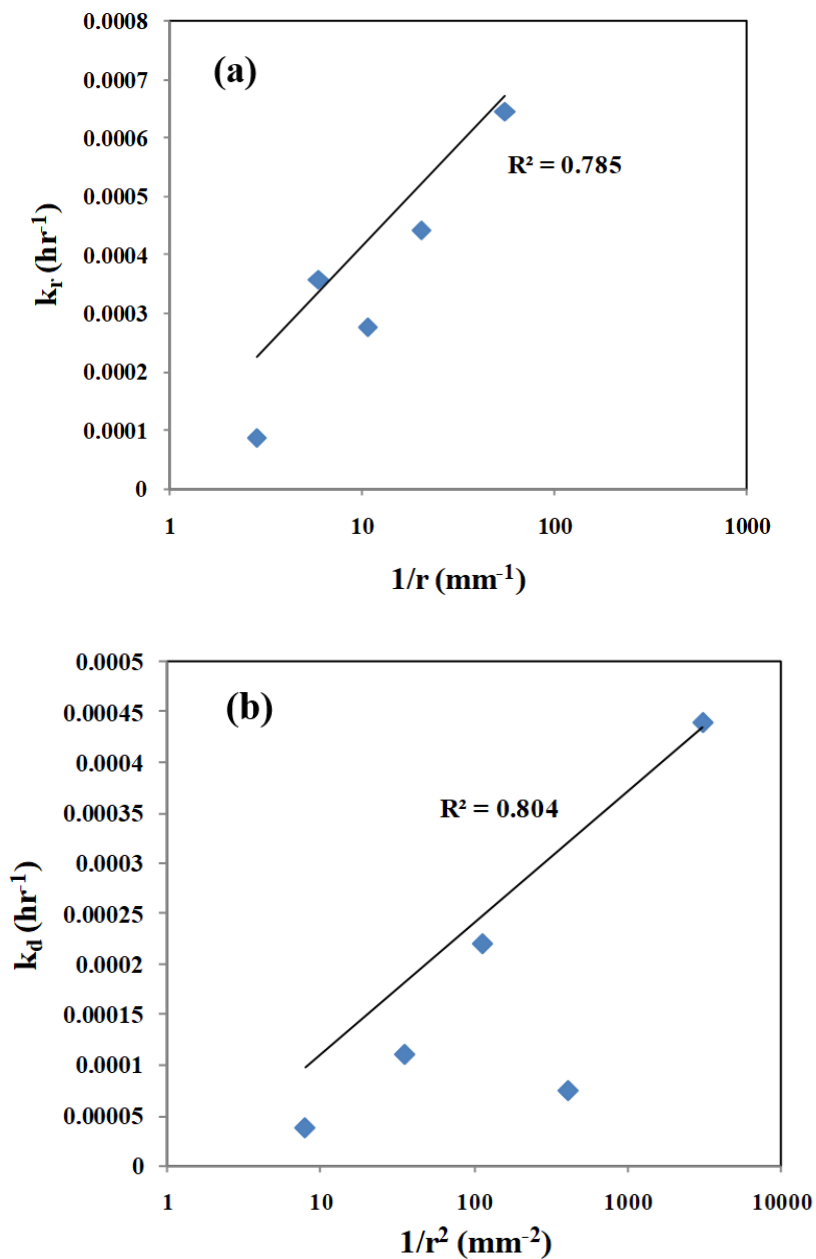


Figure S3. Plot of (a)  $k_r$  vs.  $1/r$ , and (b)  $k_d$  vs.  $1/r^2$

**Table ST1. Correlation between different physicochemical characteristics**

	<b>BD</b>	<b>pH</b>	<b>Porosity%</b>	<b>OM%</b>	<b>Sand%</b>	<b>Silt%</b>	<b>Clay%</b>
<b>BD</b>	1.00						
<b>pH</b>	-0.07	1.00					
<b>Porosity%</b>	-0.95	0.29	1.00				
<b>OM%</b>	-0.29	0.48	0.44	1.00			
<b>Sand%</b>	0.12	0.89	0.05	0.39	1.00		
<b>Silt%</b>	0.19	-0.91	-0.36	-0.64	-0.93	1.00	
<b>Clay%</b>	-0.81	0.25	0.86	0.78	0.04	-0.41	1.00