Acidic heap leaching behavior of uranium from El-Sela area, South Eastern Desert, Egypt

Mohamed S Nagar (✉ mf_nagar@yahoo.com)

Nuclear Materials Authority

Walid M Morsy

Nuclear Materials Authority

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Abstract

The column percolation technique was used to examine the leachability of uranium from El-Sela uranium mineralization. The agglomeration effect, particle size, flow rates, acid concentration, solid to liquid ratio, and sand agglomeration effect were all studied in the kinetics of uranium leaching. The acidic leach solution causes alteration and thus dissolves the oxides that fill joints and fractures, resulting in a reduction in ore particle size, as well as the swelling of fine particles caused by acid leaching over time. As a result, the focus of this research is on the possibility of increasing the permeability of ore heaps by adding cobblestone. At a height of 3.0 m within the column, the optimal ratio of cobblestone to ore was found to be 1:4, and the irrigation rate was reduced from 0.15 to 0.1 L/m²/min, increasing the uranium dissolution efficiency from 47.5 to 79 percent. Finally, the column leaching efficiency is confirmed by fitting data from an application first-order kinetic law with data collected.

1. Introduction

Heap leaching is an industrial mining method that extracts precious metals by slowly percolating a leaching solution down into an ore heap. Temperature, flow rates, particle size distribution, and pores distribution, as well as ore mineralogy, all have an impact on this process. In order to achieve effective uranium heap leaching, the permeability of the stacked ore must be considered. Fine particles and clays are often the cause of clogging in heaps. This causes variable permeability, which can reduce the efficiency and homogeneity of the leaching process [1]. However, after leaching, newly formed fine particles flow downwards through the pore space among coarse particles and are deposited at local areas under the combined action of multiple factors such as hydraulic force, gravity, and chemical reactions, and a specific amount of fine particles are transported out of the reactor by the solution [2,3]. The permeability of the leach and even percolation of the lixiviant solution in the ore are the most critical aspects of heap leaching. Excessive fines produced during the leaching process, as well as their mobilisation and thus the presence of acid-consuming clay minerals, clog natural flow channels and form impermeable layers within the heap, restricting lixiviant percolation and reducing permeability, which could have a negative effect on percolation, particularly over long periods of heap leaching. It may also obstruct a regular supply of solution through the heaps. This results in poor interaction between the ore and leach solution, producing inadequate metal recoveries, or the necessity to increase the leach time.

Fine mineral particle agglomeration is usually would not minimize or eliminate poor permeability issues caused by the fine particles which tend to enhance heap leaching performance [4-6]. This process allows adjusting the particle size distribution by gathering fine particles, using mostly capillary forces, cohesion forces between particles and adhesion forces (e.g. hydrogen bonds, electrostatic and Van der Waals forces). This process may be thanks to improving the heap permeability and to reducing fine particle migration during leaching [7-9].

Acid agitation and column leaching with sulphuric acid were used in many chemical experiments on El-Sela mineralization, followed by recovery using IRA-400 and D236B anion exchange resin [10, 11]. Using a shrinking core model with diffusion control through a porous product layer, the experimental data from the leaching of uranium from El-Sela uranium ore with hydrochloric acid solution were well interpreted [12]. Column leaching experiments will be investigated in this study first to see if they can be used as a heap leaching technique.

Geology and Mineralogy of El-Sela uranium mineralization

El-Sela region is situated in the southern part of Egypt's Eastern Desert, near the Sudan border, 22 kilometres Southwest of Abu-Ramad city as shown in Figure 1. Many authors studied the area geologically, mineralogically, geochemically, and radiometrically as part of their study of the Eastern Desert's uranium potentiality in granites, concluding that El-Sela granite is a highly fractionated high-K calc-alkaline (HKCA) magma containing primary muscovite and occurring as a medium-sized granite pluton affected by high alteration [13]. They also discovered that uranium mineralization such as uranothorite, high U-monazite, and high U-zircon.

The geochemical data will determine the characteristics of the study uranium fertile granites. The uranium fertility depends essentially on the typology of their host granites. Peraluminous, high-K and low Na and Ca contents are the main indicators of the U-fertility of granites. Under certain conditions of alteration, the high-K calc alkaline (HKCA) granites can form uranium ore with less tonnage [15]. In mineral exploration, the alteration halos around ore bodies in altered zones are used as primary guides. Depending on the type of U-deposit, important alteration types accompanying uranium mineralization develop alteration minerals such as chlorite, albite, silicate minerals, sericite, clay, and illite [16]. On the other hand, the data of XRD pattern (Figure 2) showing the peaks of goethite, cryptomelane and quartz as constituents of the uraniferous manganese oxide. According to geochemistry and mineralogy of El-Sela granite presented above, it's obvious that, the weakness of ore bonds and joints lead to be destroyed and moldered during crushing process.

2. Experimental

2.1 Sampling

The rate of leaching is influenced by the particle size. To prepare the samples for agitation and column leaching tests, they are crushed into a different particle size. This particle size meets the requirement that the real particle diameter does not exceed 1/10 of the inside diameter of the column [17]. The size distributions of a representative sample are shown in Table 1.

Table 1: Size distribution of operated samples

Particle size, mm	Weight, kg	Weight percentage, %
-30~+20	10	50
-20~+10	7.5	37.5
-10~+5	2.5	12.5

2.2. Ore agglomeration Procedure

Water and sulfuric acid were used to agglomerate the uranium mineralization at El-Sela. For the agglomeration experiment, an El-Sela uranium mineralization feed charge of 20.0 kg dry ore with a known amount of H_2SO_4 binder was used. This loading is approximately 10-15% of the total effective drum size. Before being moved into the drum granulator, the powder was pre-mixed with a pre-determined volume of acid in an acid resistance glass ware for 10 minutes. A cumulative batch time of 30 minutes was used for the majority of the agglomeration samples..

2.3 Agitation Leaching Experiment

Crushed to a grain size of approximately "-100 mesh" was a representative sample from the El-Sela field (-0.15mm). Because of the natural of chemical composition of the study sample, the acid agitation leaching technique was chosen for this study. Except for the study element, all of the leaching experiments were carried out under the same general conditions: 250 gm sample, 50 gm/l acid concentration, 1/2 S/L ratio, room temperature (25°C), and a 6 hour contact time. The uranium content of the final agitation leaching residue was also determined.

2.4. Column experiments

To determine the optimum leaching parameters for the treatment of the El-Sela samples, a series of column tests were conducted. For the first part of these experiments, small PVC columns (100 mm internal diameter and 1500 mm height) were used (agglomeration and non-agglomeration testes). The column was flushed with fresh water before the acid leaching to remove any soluble phases that may have developed during sampling and storage. The rate of percolation could be stabilized and the column's permeability could be determined using this method. Columns are run for 16 days or until very low uranium concentrations appear in the pregnant solution, after which experiments are run to see what impact the following parameters on uranium leaching, as ore particle size, application flow rate, lixiviant acid concentrations and consumption.

The second part of this work to study the effect of cobblestone addition in which, cobblestone of the same size of the ore sample was distributed along four columns (A, B, C, and D) as sheets to allow the resulted fines to agglomerate on it, where the ratio of 1/3, 1/4, 1/5, and ore without cobblestone were tested. Three different flow rates were testing (one for every column) 0.15, 0.10, and 0.05 L/m²/min. Samples from pregnant leach liquor were taken, and their uranium content, pH, and other impurities are

analyzed to determine if the effluent should be recycled as intermediated leaching solutions (ILS) or transferred to recovery circles pregnant leaching solution (PLS). Leaching can be steeped if the value of the extracted uranium is less than the cost of operation. Of course, if a technical indicator like leaching efficiency is the only thing that matters, then leaching can continue.

2.5 Analytical Method

Under different conditions, uranium was analysed in the corresponding solutions using Arsenazo III reagent [18]. A Lambada UV/VIS spectrophotometer (Perkin-Elmer, USA) was used for this purpose. Prior to titration, uranium was analysed using an oxidimetric titration process against ammonium meta vanadate in the presence of diphenylamine sulfonate indicator; proper uranium reduction was accomplished using ferrous sulphate [19].

3. Results And Discussion

3.1 Chemical composition of El-Sela uranium mineralization

The chemical composition of studied uranium mineralization sample was found sufficiently simple assay is low in CaO (0.6%) and MgO (1.1%) as shown in Table 2. In addition, the silicic gangue minerals (feldspars and quartz) equivalents to 71.6% SiO₂ are frequently predominating and which are practically inert to acid attack. The other major oxides; namely Al₂O₃, Na₂O and K₂O assaying 15.15, 0.07 and 1.08% respectively are mainly present in the feldspar minerals. The presences of Fe₂O₃ and MnO in relatively high percent (5.37 and 0.75 respectively) enhance the uranium dissolution, since act as an oxidizing agent during the leaching process. In other hand, the presence of P₂O₅ have harmful effect during leaching if pH exceed 2.0.

Table2: The main chemical composition of the ore sample.

Oxides	P ₂ O ₅	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	MgO	CaO	Na ₂ O	K ₂ O	L.O.I
Wt, %	0.33	71.61	15.15	5.37	1.44	0.75	1.1	0.6	0.07	1.08	2.1

3.2 Agitation Leaching tests

El-Sela mineralized samples with 700ppm U were subjected to uranium agitation leaching in the lab under a variety of conditions to determine the optimum conditions that lead to high uranium leaching results. The following conditions were used to test cost savings as well as high kinetics: 50g/l sulfuric acid concentration, 6.0 hours as agitation time, ore size of -0.15mm, solid/liquid ratio of 1/2, and room temperature [11].

3.2 Results of column leaching (percolation)

Uranium dissolves in three stages during column leaching studies. The first release results when the column is flushed with water. During the acid leaching of the column, two further uranium releases occur: a rapid dissolution as soon as the pH decreases, followed by a slower dissolution at the end of the leaching process.

3.2.1 Effect of agglomeration

That process is the pre-mixing of the operated sample with lixiviant solutions at atmosphere temperature as shown in Figure 3. It improves the permeability of the ore [20]. In some times, agglomerates can be made stronger by adding a binder to the water [21]. Then agglomerates weathered for maturation a time period ranging from 14 to above 300 hr [22]. Two kilograms of crushed ore have been agglomerated during 5.0 min with a L/S ratio of 1/10. In addition, a ratio of 20 kg/t has been used for sulphuric acid as binder.

As shown, in Figure 4, the agglomeration processes enhance the leaching kinetics and improve its dissolution performance at the first leaching period. The agglomerated sample gives the highest dissolution rate of uranium (45.5%) in a shorter time (11 days) than the non- agglomerated sample (40.2% uranium dissolution in 16 days). With time the leaching rate of agglomerated ore will resemble the behavior of non-agglomerated ore, which owing to the leaching resistance increases with time.

3.2.2 Effect of grain size

Three different particle sizes of El-Sela uranium mineralization have been studied; namely, -40, -20 and -10mm. As shown in Figure 5, it's noticed that, the overlap between the leaching curves which owing to the alteration induced by acidic leach solution. Since, dissolve the oxides filling joints and fractures which lead to reducing the particle size of ore, in addition to the swelling of fine particles induced during acid leaching with time.

3.2.3. Effect of free acidity

The mineralogical and chemical composition of mineralized samples plays an essential role in the free acidity of leach solutions and its consumption. Acid concentrations range derived from batch experiment; about 30~50 g/L was tested in this experiment as shown in Figure 6.

As the acidity of lixiviant solutions increase, it's the redox state increase that leads to the solubility of uranium is increased indeed dissolves iron oxides, which enhances recovery efficiency. On another side, increasing acidity of the lixiviant solution (30 g/L to 50 g/L of H_2SO_4) leads to higher silicate dissolution which has a bad effect on leaching performance and acid consumption. Sulfuric acid concentration leads to greater acid consumption and volume of lixiviant to be handled, essentially due to stronger silicate dissolution and secondary precipitation.

Predicting chemical reactions and reagent use during the leaching process can be achieved using the pH values obtained from pregnant leach solutions. Figure 7 represents the transition in pH values of the

pregnant leach solution over time. The sulfuric acid adsorbs on the mineralized sample for a short period of time, resulting in a pregnant leach solution with a high pH, which gradually decreases with time.

In general, the recycling of the intermediate pregnant solution (IPS) has little change in the acid consumption and the lixiviant volume. When the IPS is recycled after adjusting the pH, the uranium concentration was increased due to its higher Fe^{3+} content which accelerate the uranium dissolution.

3.2.5. Effect of flow rate, L/m²/min

The flow rate of the solution also influences uranium recovery. As shown in Figure 8, the flow rate shows little effect on uranium recovery due to the decrease in permeability induced with time, which come from the swelling of clay minerals which lead to decrease pores between grains. The maximum uranium dissolution after 15 days leaching at 0.15L/ m²/h flow rate was 48.5%.

3.3. Effect of clay minerals on the permeability of solution during heap leaching

Owing to the presence of clay minerals in high percent, there are some limitations which include slowing down the process, the suitable porosity requirement of the leachate ore, and the poor attack of acidic solutions on refractory ores. The swelling of clay will negatively affect the porosity and permeability of solution. The clay minerals have also the ability to adsorb positively charged metals onto their surfaces as well as adsorbing metals by the interlayer substitutions.

The initial crack network in the particles increases during the leaching process, which splits every single particle into two or more new ore particles and produces a particle size distribution different from the initial reactor feed [19]. Excessive amounts of the fines generated during the leaching process and their mobilization would result in reduced permeability as the leaching process progresses, which could have a negative effect on percolation especially over long periods of heap leaching operation. It would also prevent a uniform flow of the solution through the heaps which leads to poor interaction between the ore and leach solution, producing inadequate metal recoveries, or the need to extend the leach time.

3.3.1 Improvement of the leaching efficiency of uranium

The first agglomeration process is split with time by the leaching effect so that we need to solve that problem during leaching. The fines split during leaching can reclog the heap again, so that we need to put small sheets of strong cobblestones along the column to be agglomerated on them and keep the kinetics stable during leaching and choose the appropriate flow rate to spray over the ore materials, also, choosing the height of the ore inside the column, which gives the highest percentage of extraction in the presence of cobblestone.

3.3.2 Effect of cobblestone ratio addition on uranium extraction

The cobblestone of the same size as the ore sample was distributed along with four columns (A, B, C, and D) as sheets to allow the resulted fines to agglomerate on it. In leaching columns the ratio of cobblestone

to ore sample was as followed; A=without, B=1/5, C=1/4, and D= 1/3. As shown in Fig.9 it's obvious that the sand sheets have a favorable effect on kinetics; since the kinetics increases as sand ratio increase owing to the porosity increase until the ratio of 1/4 sand/ore ratio, at column D (1/3) ratio leaching efficiency tends to decrease which owing to the disproportion between the irrigation flow rate and created permeability. It's noticed that as the ratio of 1:4 sand (cobblestone) to ore the permeability increased uranium leachability increased from 48.5 to 73% in 16 day leaching period at flow rate of 0.15L/m²/min.

3.3.3 Effect of irrigation flow rate after cobblestone addition

As we explained previously, there is no effect of the flow rate on the rate of uranium extraction before adding sand, due to the decrease in permeability induced with time, come from the swelling of clay minerals which lead to decrease pores between grains. In this part, we are exposed to the effect of the flow rate on uranium extraction after adding sand by 1/4. Three different flow rates were testing (one for every column) 0.15, 0.10, and 0.05 L/m²/min. The results show that an increase in the irrigation rate leads to a decrease in the permeability and the uranium recovery reach to 70 % in 17 days at an irrigation rate of (0.15L / m² / min) compared to a recovery of 77.3% at an irrigation rate of (0.1L / m² / min) for the 20-day leaching period as shown in Figure10. This low rate prevents the accumulation of solutions on the heap surface and allows free air entry through the heap.

3.3.4 Effect of column height after cobblestone addition

In a previous study, the effect of the ore height in the column dissolution rate of uranium from El-Sella ores was studied, and the results indicated that the lowest uranium extraction was obtained at 3.0 m column height without treatment or addition of permeable materials [11]. In order to determine the effect of ore height using the above cobblestone addition and 0.1L/m²/min scheme. Three column tests were conducted with (2.0, 3.0, and 4.0 m) ore height. Figure 3 demonstrates that uranium dissolution increased as the column height decreases. Therefore, the lowest uranium dissolution was achieved in the 4-meter high column. While in the case of 2 and 3 meters, the process of dissolving uranium is very close, which is about 79% for the 20 day leaching period.

3.4. Verification of kinetic model

The data of leaching experiments were discussed with two different approaches of the first-order kinetic model. As presented in the following equations;

$$X_t = X_{\infty}(1 - e^{-kt}) \text{ as a derivative of } X_t = X_0 e^{-kt} \quad \text{first order law}$$

Where X is uranium leached fraction at Time t, X_{∞} = maximum uranium leached fraction at $t = \infty$ X_0 is the initial uranium fraction at, k is rate constant and Time t, day [23,24].

The results of the test were evaluated with a general time dependent kinetic model and a modified kinetic model based on the ratio of the reagent consumption volume per mass of the initial valuable uranium.

As shown in figure 11, the column C (with sand cobblestone) gives linear relation between uranium leached fractions than column A (without sand cobblestone). From above Figure the rate constants for two columns has determined then used in calculation to predicted data on basis of above first order law.

As shown in figure 12 (A, C), there are the large deviation between experimental and calculated data in column A .On the contrary, in column C, there are a closeness between them with linear relationship between leached values. Thus, the column C with cobblestone show good leaching behavior in comparison with column A which appear bad behavior on column leaching.

4. Conclusion

Acid leaching of uranium from El-Sela low-grade uranium mineralization induces alteration by dissolving the oxides filling joints and fractures which lead to reducing the particle size of ore, in addition to the swelling of fine particles induced during acid leaching with time. Improved permeability with the addition of cobblestone would lead to increased permeability and leaching efficiency to 79%. Experiment data was fitted with a first-order kinetic model and also modeled based on the reagent consumption per mass of the initial valuable species. Both approaches of the first order kinetic model provide a good agreement with the column test data, which benefits the process planning of uranium heap leaching.

Declarations

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

Detailed geologic map of El Sela shear zone, South Eastern Desert of Egypt modified after [14]

Figure 2

X-Ray Diffraction showing the peaks of goethite, cryptomelane and quartz as constituents of the uraniferous manganese oxide

a) Non agglomerated

b) during circulation

c) Agglomerated

Figure 3

Photographic images of ore sample during agglomeration process.

Figure 4

Effect of agglomeration on uranium leaching efficiency during column leaching.

Figure 5

Effect of grain size on uranium leaching efficiency during column leaching.

Figure 6

Effect of acidity on uranium leaching efficiency during column leaching.

Figure 7

pH of pregnant leach solution resulted during column leaching.

Figure 8

Effect of flow rate on uranium leaching efficiency during column leaching.

Figure 9

Effect of agglomeration on cobblestone on uranium leaching efficiency during column leaching.

Figure 10

Effect of irrigation flow rate on uranium leaching efficiency at 1/4 ratio of cobblestone

Figure 11

Effect of ore height on uranium leaching efficiency at 1/4 ratio of cobblestone

Figure 12

Plot of log uranium extracted fraction X against Time for columns A,C

Figure 13

Verification of column (A and C) leaching data with kinetic model calculated values