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Leaching of Uranium and Rare Earths Associated with Gattar (V) Uraniferous Material

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Summary: Yttrium group rare earths are commonly associated with uranium minerals which can be partially dissolved during the conventional sulphuric acid agitation leaching. Representative sample from Gattar (V) uraniferous material, Eastern Desert, Egypt, assayed 2475 uranium and 1070 μmL^{-1} of rare earths was subjected to sulfuric acid leaching for studying the ability of dissolving maximum uranium and the associated constituents of rare earths under moderate conditions taking in the consideration unaffecting the later uranium recovery processes. Acid concentration of 100 g/L without oxidant addition, 6.0 h agitation time, - 60 mesh (0.25 mm) solids grain size and leach slurry of 50% solid at $60^{o}C$ were the suitable conditions and under these conditions leaching efficiency of 97.3% and 61.5% were achieved for uranium and rare earths, respectively. When these conditions were applied upon six tons on pilot scale in batches each of 250 kg, leaching efficiencies more than 96.0% for uranium and 57.0-60.5% for the rare earths was leached out.

Introduction

Rare earth elements do not occur in its minerals as individual rare earth, but the rare earth mineral usually contains all the rare earth elements with some of them enriched by cerium group or yttrium group with the others in low concentration. However, about 95% of the rare earths occur principally in three minerals namely; monazite and bastnasite (as a resource of cerium group) and xenotime (as a source of yttrium group). In addition to these three major minerals there are several other rare earth resources which are important. These other rare earth minerals resources involve euxenite, gadolinite, apatite, pyrochlore and the non rare earth mineral resources especially that of igneous rocks containing uranium and thorium[(1)].

Sulphuric acid is widely used for uranium leaching from ores all over the world than the alkali carbonates because of its availability and low cost. On the other

hand, sulphuric acid leaching has many other advantages such as it needs only a relatively coarse particle size, normally needs a comparatively mild reagent concentration, requires shorter leaching times, usually applied under ambient temperature and atmospheric pressure, convenient for subsequent recovery process where it gives higher over all extraction efficiency[(2)].

Nitric acid and hydrochloric acid create serious disadvantages due to dissolving many undesirable impurities present in the ore as well as forming uranium complexes unsuitable for recovery by anion exchange resins. However, nitric acid is used exceptionally for high grade ores or to uranium concentrates produced by upgrading techniques, where the leaching stage can be directly followed by a proper solvent extraction. On the other hand, chloride leaching has been thoroughly investigated for carnotite ores (uranium-vanadium ores) and should be considered when uranium can be recovered by proper solvent extraction[(3)].

The use of external oxidant is essentially required if uranium exists in its tetravalent state (primary minerals) since only hexavalent state (secondary minerals) is readily soluble. The most common effective oxidants include manganese dioxide, sodium or potassium chlorates hydrogen peroxide, Caro′s acid (H_2SO_4 + H_2O_2), ferric iron, and oxygen. The cheapest available oxidants are usually sodium chlorate and manganese dioxide; however the later may be used in the form of pyroluosite mineral which contain 65–70% MnO_2. On the other hand, using hydrogen peroxide or Caro's acid as oxidant would eliminate the presence of the heavy metal manganese, beside they have a mineral wastage criterion[(4)]. Ferric iron is actually one of the most effective oxidants in sulphuric acid leaching, especially if phosphate ions are present, as it prevents the formation of uranyl phosphate complex which would render subsequent uranium extraction relatively difficult[(5)]. Generally, iron is present in the ore material as iron-bearing minerals e.g. pyrrhotite, hematite or else in the form of metallic iron abraded during grinding.

Experimental

Procedure

Sulfuric acid leaching experiments were conducted to study the ability of dissolving maximum uranium and the associated constituents of rare earths from Gattar (V) uraniferous material, Eastern Desert, Egypt, under moderate conditions taking in the consideration unaffecting the later uranium recovery processes. The representative sample assayed 2475 μmL^{-1} uranium associated with 1070 μmL^{-1} of rare earths. The main factors affecting uranium leaching efficiency involving acid concentration, agitation time, leach acid to ore ratio, temperature, solids grain mesh size and the amount of oxidant (H_2O_2) addition. The experiments were conducted using 100 g of the solid material and good agitated with the leaching acid without splashes in a 250 mL glass beaker using digital mechanical stirrer at 200 r.p.m.

After each experiment, the leach slurry was filtered out using Whatman 41 filter paper and the leach liquor was analyzed against both uranium and rare earths. Leaching efficiency percent was calculated according to the following equation:

$$\text{Constituent leaching efficiency, \%} = \frac{\text{Leached constituent}}{\text{Original}} \times 100$$

Methods of Analysis and the Instruments

Uranium was determined by Redox Titrimetry[6] and rare earths were analyzed by Arsenazo III[7], using UV-spectrophotometer “single beam multi-cells-positions model SP-8001, Metretech Inc., version 1.02, 2000/10/01, with glass cell of 10 mm”.

Results and Discussion

Constituents of the Raw Material

Gattar (V) mineralization located at 35 km west of Hurghada city Eastern Desert, Egypt. It is situated in the Hammamat sediment directly in contact with altered younger granite and considered one of the most interesting uraniferous areas. This ore material is composed of 30% feldspar, 40% quartz, 10% clay minerals,

7% iron oxides, 5% carbonate minerals and 8% other minerals[8]. This mineralization contains yttrium group rare earths where the yttrium element represents 55% of the total rare earths[9]. Results of leaching efficiencies for both uranium and rare earths from this uraniferous material were shown in Table (1) and would be herein discussed.

Effect of Sulphuric Acid Concentration

Acid concentrations from 60 to 150 g H_2SO_4/L were studied where the other prevailed conditions were - 60 mesh ore material particle size, 6.0 hours leaching time at ambient temperature (about 25^oC), 50% solids to the leach acid and without oxidant addition. It is obvious from the obtained results that the solubility of uranium increases with increasing the acid concentration from 60 to 125 g H_2SO_4/L where the leaching efficiency was 70.1% and 96.1% for uranium while that of rare earths was 39.1% and 47% respectively. There is no increase in the leaching efficiency at acid concentration more than 125 g H_2SO_4/L for those elements.

The acid concentration of 100 g H_2SO_4/L considered a suitable moderate concentration for leaching, where the increase in the leaching efficiency from 100 to 125 g H_2SO_4/L was only 0.8% and 0.4% for uranium and rare earths respectively. However, using high acid concentrations led to the dissolution of undesired impurities, especially iron which interfere the final uranium product as well as the subsequent steps for rare earths recovery. On the other hand, to avoid neutralization of the residual free acid during the subsequent extraction processes of uranium.

Effect of Agitation Time

The effect of agitation time on uranium and rare earths leachability from Gattar (V) ore material was studied to identify the necessary time required for solubility of the required elements as maximum as possible. The effect of agitation time on leaching efficiency was conducted for a time ranging from 1.0 to 8.0 hours under the conditions of ore particle size of - 60 mesh size, 100 g

H_2SO_4/L, 50% solids to the leach acid and agitating the mixture at ambient temperature (about 25^oC) without oxidant addition.

The obtained leaching efficiency data (Table 1) reveal that a substantial amount of uranium and rare earths was leached after 2.0 h and reached to its maximum after 8 h. In this regard, the leaching efficiency was increased from 84.2% to 96.4% for uranium and from 41.3% to 46.9% for the rare earths, respectively. Above the period of 6.0 h there was only a slight increase in solubility of both uranium and rare earths, where the increase in the leaching efficiency was 1.4 and 0.3%, respectively, consequently, leaching of Gattar (V) ore material for 6.0 h is adequate.

Effect of Solid/Liquid Ratio

The effect of solid ore/leach acid ratio from 50 to 60% were studied under the conditions of ore material - 60 mesh size, 100 g H_2SO_4/L without oxidant addition and agitating the slurry mixture for 6.0 hours at ambient temperature (about 25^oC). From the results of leaching both uranium and rare earths (Table 1) it is clear that the efficiency decreased with increasing the solids ratio from 50 to 60%, where the efficiency was decreased from 95 to 85.9% for uranium and from 46.6 to 40.1% for rare earths, respectively. This indicates that some of the acid was consumed by the excess amount of solids which contains 5% carbonate minerals as previously mentioned. However, it would be economically to use high solid to leach acid ratio[3], so the acid concentration would be corrected to be equivalent that could be used at the ratio of 50% solids.

Table (1): Results of Lab Scale Leaching Efficiencies for both Uranium and Rare Earths from Gattar (V) Uraniferous material

Leaching Factor	Leaching Efficiency, %	
	U	REE
Sulphuric Acid Conc., g/L		
60	70.4	39.1
75	84.1	43.3
100	95.3	46.6
125	96.1	47
150	96.1	47
Agitation Time, h		
2	84.2	41.3
4	89.8	43.2
6	95.3	46.6
8	96.4	46.9
Solid/Liquid Ratio, %		
50	95.3	46.6
55	88.7	43.2
60	85.9	40.1
Ore Particle Size, mesh		
60	95.3	46.6
100	97.2	51.6
150	97.7	57.8
200	98.2	61.3
Oxidant, mL		
0	95.3	46.6
0.5	95.4	47.0
1	96.2	47.8
2	96.3	48.4
Temp., ^{o}C		
25	95.3	46.6
50	96.1	54.8
60	97.3	61.5
70	97.8	68.3
80	98.1	73.7

Effect of Ore Particle Size

Particle size of the ground uranium ore would make it amenable for leaching due to increasing the solids surface area exposed to attack with the leach acid. The effect of Gattar (V) ground ore particle size has been studied using samples having a size varying from - 60 to - 200 mesh size (- 0.15 to - 0.063 mm) under the conditions of 100 g H_2SO, leaching for 6.0 hours agitation time at ambient temperature, 50% solids to the leach acid and without oxidant addition. From the

results (Table 1), it is obvious that leaching efficiency increased by 2.9 % (from 95.3 to 98.2%) when particle size of the ore was decreased from – 60 to – 200 mesh for uranium and by 14.7% (from 46.6 to 61.3%) for the rare earths respectively. It is worth to mention that more grinding would increase the dissolution of many gangue constituents as well as complicating the filtration and washing steps in addition to the costs of the grinding step itself as previously mentioned. However, particle sizes of - 60 mesh considered the suitable and confidant size to perform the leaching[3].

Effect of oxidant addition

The effect of an external oxidant addition on uranium and rare earths leachability from Gattar (V) ore material was carried out to identify the enhancement of their solubility. The effect of oxidant addition (0.0 – 2.0 mL H_2O_2/100 g ore) on leaching efficiency was conducted under the conditions of ore particle size of - 60 mesh size, 100 g H_2SO_4/L, 50% solids to the leach acid and agitating the mixture at ambient temperature (about 25^oC) for 6.0 h. Leaching efficiencies for uranium and rare earths obtained from these experiments (Table 1) showed that there was no significant improvement above that verified without using oxidant indicating that, at least most of the uranium minerals are present in their oxidized state.

The manner of uranium leaching in the absence of an oxidant has actually been expected with respect to the mineralogy of the uraniferous material which indicated that more than 90% of uranium was present as secondary uranium mineral "uranophane", while sooty pitchblende (the primary mineral plus its alteration products) is only present in a minor amount i.e. the ore is mainly of the secondary or oxidized type. The remained insoluble uranium is possibly present as primary uranium minerals and/or refractory minerals e.g. zircon, uranium association, etc.[8].

Effect of Temperature

In general, it is advisable to apply ambient temperature during leaching because it would minimize dissolution of many gangue constituent in the leach liquor specially iron which would lead to a lot of problems in later uranium recovery steps beside saving in energy costs. The effect of temperature on Gattar (V) ore leaching efficiency was however studied in the range from 50 to 80^{o}C under the conditions of 100 g H_2SO_4/L, ore material particle size of - 60 mesh size, 6.0 hours leaching time, 50% solids to the leach acid and without oxidant addition.

From the results (Table 1), it is clear that, the leaching efficiency of uranium slightly increased by 2.8% at 80^{o}C from that at ambient temperature while this efficiency was greatly enhanced by 27.1% for rare earths leaching. Taking in consideration that increasing the temperature enhances solubility many of the other undesirable impurities such as iron oxides, phosphates, clays, silicates, chlorites etc.[10] in addition to the economical considerations. It is advisable to conduct the leaching step economically at 50 – 60^{o}C through the heat of dilution provided from the addition of the required amount of concentrated sulphuric acid directly to the slurry of the solids ore material and water mixture and also the heat generation due to decomposition of the associated carbonates. Accordingly, the leaching efficiency can be increased by about 2% for uranium and 8.2–14.9% for the rare earths.

Pilot Scale Leaching Experiments

Six tons of Gattar (V) uraniferous material were leached, in batches each of 250 kg, under the pre-mentioned conditions (100 g H_2SO_4/L acid concentration, - 60 mesh "0.25 mm" solids grain size, 6.0 hrs agitation time at about 50^{o}C and slurry of 50% solids without oxidant addition). Results of these experiments are tabulated in table (2) from which it is clear that more than 96.0% of uranium and 57.0 - 60.5% of the rare earths constituent were leached out.

Table (2): Results of Pilot Scale Leaching Efficiencies for both Uranium and Rare Earths from Gattar (V) Uraniferous Material

Concentration in Leach Liquor, μmL^{-1}		Leaching Efficiency, %	
U	**REE**	**U**	**REE**
853	243	95.4	54.7
877	302	96.1	56.2
937	331	96.8	58.1
997	337	97.3	59.6
Mean **916**	**303**	**96.4**	**57.2**
912	346	96.5	58.4
932	354	96.7	57.8
1150	484	97.1	59.5
1369	423	97.3	55.3
Mean **1090**	**402**	**96.9**	**57.8**
845	320	94.7	56.1
910	338	95.9	59.7
980	355	97.0	58.5
1015	382	96.4	59.6
Mean **962**	**349**	**96.0**	**58.5**
1567	579	96.2	60.4
1695	676	97.1	61.0
1805	798	95.8	59.7
2598	926	97.3	60.8
Mean **1916**	**775**	**96.6**	**60.5**
1230	442	95.7	61.6
1428	549	96.3	58.3
1626	566	96.9	60.7
1805	623	97.2	59.8
Mean **1522**	**545**	**96.5**	**60.1**
992	400	95.8	56.4
1278	586	97.3	58.2
1607	617	96.7	59.9
1695	631	97.1	61.3
Mean **1393**	**559**	**96.7**	**59**

Conclusion

Leaching conditions of 100 g H_2SO_4/L acid concentration, - 60 mesh (0.25 mm) solids grain size, 6.0 h agitation time at 60^oC, slurry of 50% solids without an oxidant addition are considered satisfactory for leaching of both uranium and rare earths from Gattar (V) mineralization without affecting the later extraction processes of uranium. Under these conditions and with regarding to the addition of concentrated acid directly to the slurry leaching efficiency of 97.3 and 61.5% for uranium and rare earths respectively could be achieved. When these conditions were applied in pilot scale, leaching efficiencies more than 96.0% for uranium and 57.0-60.5% for the rare earths was achieved.

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