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Effect of peroxodisulfate on uranium leaching with ammonium bicarbonate

In this study, uranium leaching from ore material using acid solution and bicarbonate in a presence peroxodisulfate ion was examined. For experiments two different tips of leaching methods were used: leaching in static and dynamic conditions. The determination of uranium concentrations in product solutions were analyzed by titrimetric (by ammonia vanadate solution) method. The maximum yield of uranium leached with ammonium bicarbonate in a presence of ammonium peroxodisulfate (5 g/L) was only 33%, which is half the corresponding value obtained by sulfuric acid (65%).

Keywords: Uranium leaching, ammonium bicarbonate, sulphuric acid, in-situ methods, agitation leaching, dynamic leaching.

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Влияние пероксодисульфат-иона на степень извлечения урана растворами гидрокарбоната аммония

В работе приводятся результаты исследования выщелачивания урана разбавленными растворами серной кислоты и гидрокарбоната аммония в присутствии пероксодисульфат-ионов. Максимальное извлечение урана гидрокарбонатом аммония в присутствии пероксодисульфат-иона достигает 33%, что составляет половину от извлеченного растворами серной кислотой (~65%).

Ключевые слова: выщелачивание урана, бикарбонат аммония, серная кислота, методы подземного выщелачивания, агитационное выщелачивание, динамическое выщелачивание.

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Ураны аммоний гидрокарбонатының ерітінділерімен шаймалауға пероксодисульфат-ионның әсері

Жұмыста ураны күкірт қышқылының және аммоний гидрокарбонатының сұйытылған ерітінділерімен пероксодисульфат қатысында шаймалау нәтижелері келтірілген. Пероксодисульфат-ионының қатысында аммоний гидрокарбонатымен шаймалау кезінде уранның максималды шығымы 33%-ды құрады, келтірілген көрсеткіш ураны күкірт қышқылының ертіндісімен шаймалау кезіндегі шығымның (~65 %) тек жартысын құрайтындығы анықталды.

Түйін сөздер: ураны шаймалау, аммоний бикарбонаты, күкірт қышқылы, жерасты шаймалау әдісі, агитациялық шаймалау, динамикалық шаймалау.

Introduction

Uranium minerals occur in the siliceous rocks and sedimentary deposits, as a mixture of low solubility quadravalent species and soluble hexavalent species. uranium [1,2]. Uranium ore is mainly associated with minerals in form of carnotite, coffinite, and occasionally uraninite in sites where uranium in-situ leaching used [3].

Uranium leaching is a complicated heterogeneous process, which can be carried out in kinetic and diffusion regimes [4]. At present sulphuric acid and carbonate are used for injection in uranium deposits, which cause a number of chemical reactions between liquid and porous walls among which two main reactions can be distinguish [5]: the *useful reactions* and the *detrimental reactions* that lead to the precipitation of low solubility minerals, and decelerates the useful reactions by clogging the pores and reducing the contact surface of useful reactions.

Uranium extraction by in-situ methods involving underground leaching using diluted sulphuric acid solutions has been conducted in Kazakhstan since the 1970s [6]. Over the years, significant improvements have been made on the leaching techniques employed to extract the uranium from the ore bodies. Many physico-chemical studies on the effectiveness of uranium leaching using various complexing agents (sulphate, carbonate ions) and oxidants (H_2O_2, MnO_2, and others) were conducted as part of this optimisation process. Indeed, most data were only made available in internal (often classified) mining company reports, and are not generally available in the open literature.

Despite great efforts in identifying the mechanism of uranium leaching processes when using sulphuric acid as a complexing agent, some problems related to the low uranium extraction yield in certain types of rocks still remain for Kazakh mining companies using in-situ mining. Clearly, there is a need to achieve a better understanding of the interactions between in-situ leaching solutions and rock materials with a view to improving the yield of extraction of uranium into process solutions.

In this study effect of ammonium bicarbonate in a presence of peroxodisulfate ion to uranium extraction degree from ore has been determined under dynamic leaching experiments. The results were compared with the corresponding data obtained at the same conditions using sulfuric acid as a leaching agent.

Experimental

For this study typical ore samples from the southern Kazakhstan territory mining sites have been examined. X-ray diffraction analysis indicated that the ore was mainly composed of quartz and feldspar, with sand and clay as minor constituents. Uranium concentration was determined by titration with ammonium vanadate.

Agitation leaching test

Leaching was performed in conical-bottomed tanks with volumes 250 ml, which were placed on agitator to provide continuous mechanical agitation. The leaching of the ground ore was carried out in a 10 g batch and the desired amount of ore was added to 0.125 L sulfuric acid solution with concentration range from 5 to 30 mg/l. L:S (liquid to the solid ratio) was kept from 10 to 12.5. The reactor's volume decreased by 5 ml each time a sample was taken for uranium concentration.

Dynamic leaching tests

Two 50 cm long organic polyethylene columns with inside diameter 3 cm were filled with a total of 800 g ore. Sands were placed in two ends of column and tamped into place uniformly using a cylindrical tool in a single lift. The leaching columns were held horizontally during processing.

Feed solutions were place 20-40 cm above the columns and draining into the columns with resin pipe. The study ore samples were washed with distilled water prior injection of sulfuric acid and ammonium bicarbonate. Lixiviated samples were taken every 6 hours (regardless of sample volume) from the columns outlet and were split for determinations of U by titration with ammonium vanadate, dissolved oxygen by Hach HQ30d portable meter, and sulfate and bicarbonate ions by titration.

Table 1 – Characteristics of dynamic leaching tests

Density of ore in the columns	4.5 g/cm^3
Linear flow rate of acid leaching test	0.4-0.7 m/day
Linear flow rate of bicarbonate leaching test	0.4-0.5 m/day
Concentration of sulfuric acid	10 g/L
Concentration of ammonium bicarbonate in presence of oxidant (ammonium peroxodisulfate)	7 g/L 5 g/L
Dissolved oxygen concentration in sulfuric acid medium	8.92 mg/L
Dissolved oxygen concentration in bicarbonate solution	9.23 mg/L
Duration of leaching tests	72 hours

Calculations of geochemical characteristics were done according to the formulas, with details presented elsewhere [4].

Results and discussion

Static leaching test

A plot of the percentage of leached uranium against sulfuric acid concentrations are presented in Fig.1 and Table 1 on the condition that 10 g of U mineral ores was leached for 8 h at temperature 25^0C. The results indicated that the dissolution of uranium into liquid, increased rapidly with increasing acid concentrations between 5-15 g/L and more slowly between 15-30g/L (Fig 1).

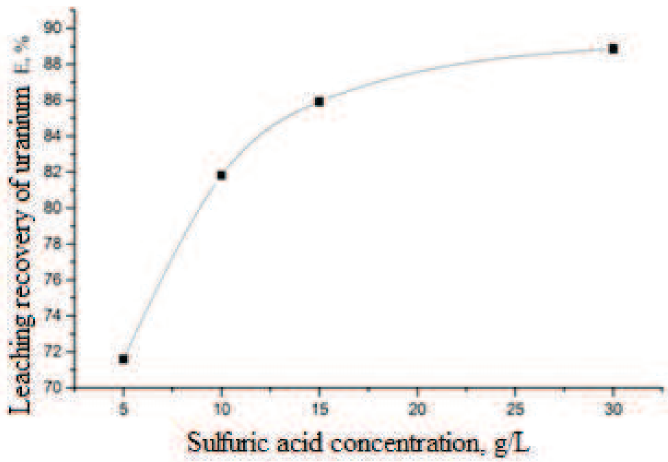

Figure 1 – Influence of various concentration of sulfuric acid solution to the recovery of uranium under static conditions

When sulfuric acid concentration increased from 5 g/L to 15 g/L, the leaching recovery proportionally increased from 72% to 86%. Increasing feed solution concentration till 30 g/L, uranium extraction degree increased only for 3% (Table 1). It was explained that further increase of acid concentration slightly effect for recovery of metal but significantly for consumption. Based on this test, the optimal concentrations of sulfuric acid for recovery uranium are in the range of 10-15 g/L.

Table 2 – Results of agitation experiments

$C_{H_2SO_4}$	Leaching time (h)	1	2	4	8
5g/L	ε, recovery of uranium, %	65	68	69	72
10g/L		64	72	77	82
15g/L		70	83	84	86
30g/L		77	88	86	89

Leaching in columns under dynamic conditions

A distinct difference was observed between change in uranium recovered during the acid leaching, compared to the uranium behavior using ammonium bicarbonate. In acid leaching column extraction yield of uranium rapidly increases after 0.3 L:S ratio than ammonium bicarbonate leaching column.

Uranium yield slows after L:S ratio reaches 2 in both leaching tests, though the difference in uranium recovery with sulfuric acid is twice higher (Fig.2 and Fig. 3). It is possible that oxidizing activity of dissolved oxygen in sulfuric acid is higher at pH 1.5-2, though oxygen was also present in bicarbonate leachate solution.

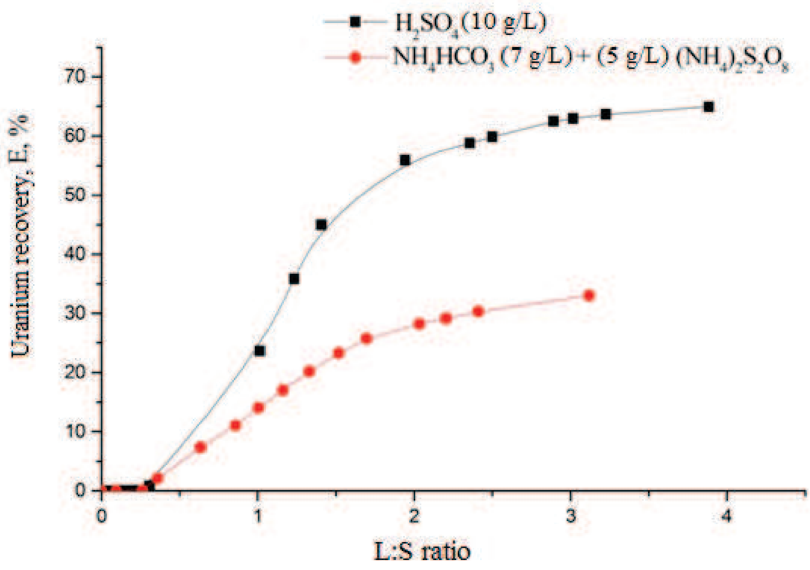

Figure 2 – Uranium recovery as function of L:S ratio

At initial steps of leaching tests in the column lixiviated with bicarbonate solution maximum uranium concentration reached than acidic, but at L:S ratio 1.2 maximum concentration leached with acid solution was about 3 times higher.

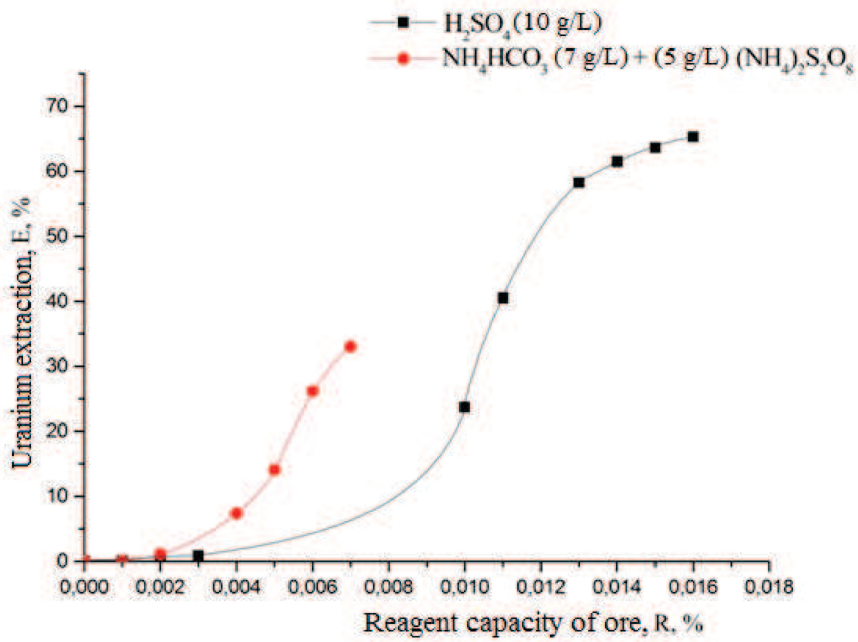

Figure 3 – Uranium yield as a function of reagent capacity of ore.

Geochemical characteristics

A plot of geochemical mining parameters of ore obtained with sulphuric acid and bicarbonate solutions are presented in Table 3 and Table 4. Average uranium concentration in acidic leachates is about 1.5 times higher than bicarbonate leaching test. As seen in Table 4 considerable quantities (65%) of uranium can be extracted by sulfuric acid solution, while 33% of uranium was extracted from the ore by ammonium bicarbonate solution in presence of oxidant. This may be due to higher oxidizing activity of oxygen in acidic medium. In contrast, reagent capacity of ore material to the ammonium bicarbonate solution was 1.7 times lower compared to sulfuric acid. This indicates that consumption of ammonium bicarbonate is lower than sulfur acid when in-situ leaching is being carried out [see Table 4].

Table 3 – Geochemical characteristics of ore by bicarbonate leaching test in presence of oxidant

Geochemical characteristics	Manners
Uranium recovery, %	33
Average uranium concentration in lixiviated samples, mg/L	58,2
L:S ratio	3
Specific consumption of solvent, kg/kg	39
Reagent capacity of ore material, R, %	0.07

Table 4 – Geochemical characteristics of ore by acid leaching test

Geochemical characteristics	Manner
Uranium recovery, %	~65
Average uranium concentration in lixiviated samples, mg/L	~92
L:S ratio	~4
Specific consumption of acid, kg/kg	~45
Reagent capacity of ore material, R, %	0.012

Conclusion

Geochemical characteristics of uranium leaching by sulfuric acid and ammonium bicarbonate have been compared. Dynamic leaching tests show higher leaching activity of sulphuric acid in uranium recovery compared to ammonium bicarbonate in presence of ammonium peroxodisulfate. It has been shown that effect of peroxodisulfate ion in ammonium bicarbonate leaching characterized by lower uranium recovery (33%) in compare with recovery by sulfuric acid (65%).Obtained data can potentially used in mathematical modeling of uranium in-situ leaching experiments.

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