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Selective Separation of Zirconium from Uranium in Carbonate Solutions by Ion Flotation

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Abstract

Separation of zirconium from uranium in carbonate media was undertaken by ion flotation. The collector chosen was octylhydroxamic acid (HOHX). It gave a well-flocculated precipitate with zirconium which floated in less than 5 min. The stoichiometry of the reaction is HOHX/Zr = 3.9/1, and the selectivity in the presence of uranium is very high. In fact, for a ratio Φ = [HOHX],M/[Zr],M, which is just stoichiometric and is close to 4, the zirconium removal rate reaches 99%, even in industrial media. The loss of uranium is only 0.5% although its concentration is 37.4 g/L. Mechanisms of separation are not affected by a variation of pH between 6.7 and 9.8, of temperature up to 60°C, and of carbonate concentration within the 15 to 60 g/L Na_2CO_3 range.

INTRODUCTION

Uranium ores contain impurities such as Zr and Mo in variable amounts depending on their origins. These impurities, along with uranium, are solubilized during acidic leaching by H_2SO_4 or during alkaline leaching by Na_2CO_3, and they are precipitated as a uranium concentrate at the end of the production cycle.

According to ASTM norms, the concentrate is either penalized (Mo/U = 0.1%, Zr/U = 0.01%) or rejected (Mo/U = 0.3%, Zr/U = 0.1%) beyond a certain limit of impurity with respect to uranium. Therefore, it is judicious to remove these impurities from the leaching solutions or from the reextraction solutions just before the precipitation of uranium, as illustrated in Fig. 1.

The subject of this paper is the separation of zirconium contained in reextraction carbonate solutions of uranium. The removal of Zr from these solutions is usually realized by hydrolysis (*1*), but this is a difficult procedure. Therefore, an attempt has been made to develop another technique called ion flotation.

Ion flotation, introduced by Sebba (*2*), is a method for the separation of soluble ionic species. It involves the formation of a precipitate in froth obtained by a flotation mechanism. The solid phase is formed by chemical reaction between the soluble species to be extracted (colligend) and an organic surface-active reagent (collector). Precipitation may occur in the solution, during conditioning, or at the liquid–gas interface during bubbling. Only the first case will be considered in this study.

Ion flotation was recently improved at the Centre de Recherche sur la Valorisation de Minerais de Nancy for uranium recovery and cadmium removal from industrial wet process phosphoric acid (*3–8*) and for molybdenum and zirconium separation from uranium in nitric and sulfuric acids (*9–11*).

EXPERIMENTAL PROCEDURE

The mechanisms of separation have been studied in synthetic solutions which simulate industrial media. The results will be applied to industrial cases.

Reagents

The reagents used were $Zr(NO_3)_2 \cdot 2H_2O$ (Prolabo); $Na_2CO_3 \cdot 10H_2O$ (Prolabo); H_2SO_4, 95% (Prolabo); NaOH pellets (Prolabo); and octylhydroxamic acid (Hoechst).

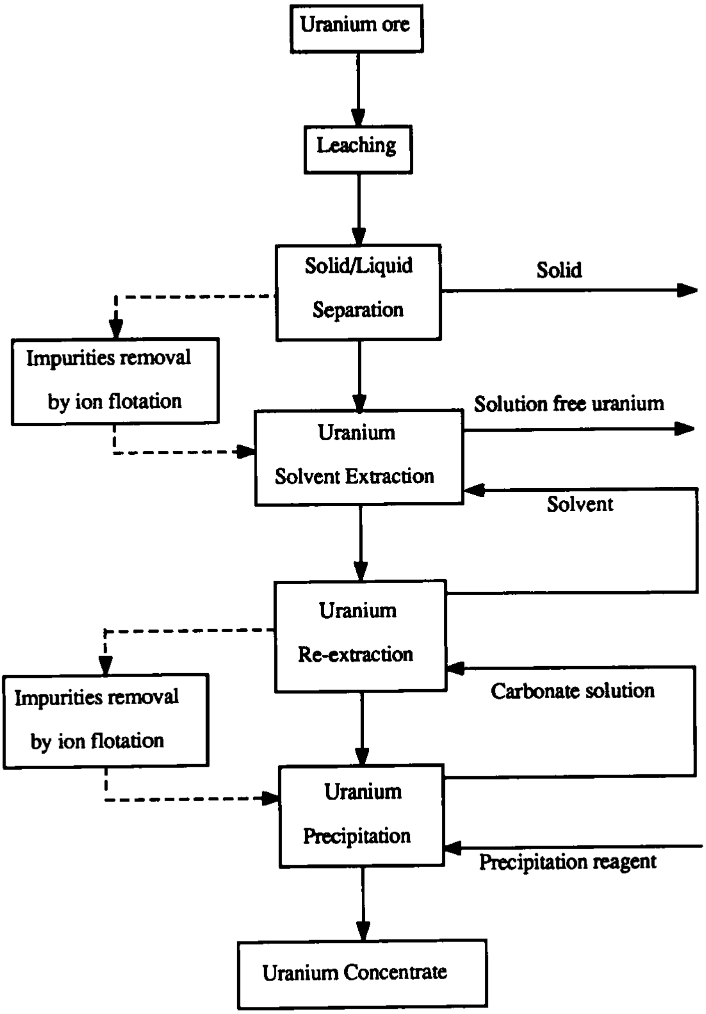


FIG. 1. Use of ion flotation for impurities removal in hydrometallurgical uranium plant.

Preparation of Solutions

Synthetic carbonate solutions of zirconium were prepared by first dissolving the required quantity of zirconyl nitrate in distilled water by the addition of 7 mL concentrated sulfuric acid per gram of Zr in order to obtain the desired concentration (C_0) in zirconium. Next, the resultant limpid solution was mixed with a carbonate solution.

The collector solution was made by dissolving the necessary quantity in ethanol or in 0.5 *M* NaOH.

Analyses

Zirconium and uranium analyses were done by I.C.P. methods.

Flotation

The flotation apparatus was described previously (*3–5*). Before beginning the flotation operation, the colligend (concentration C_0) and the collector (concentration ΦC_0) were stirred for 30 min. Upon introduction of the collector, precipitation occurs immediately. Then the solution containing the precipitate was transferred to the flotation cell and nitrogen gas was passed through the solution. The flotation operation was begun immediately and was finished when all the precipitate was collected in the foam.

The removal rate of zirconium (R %) is determined by

$$R\ \% = \frac{C_0 - C_r}{C_r} \times 100$$

where C_0 = initial Zr concentration in solution, mg/L

C_r = residual Zr concentration in solution, after precipitation and flotation, mg/L

RESULTS AND DISCUSSION

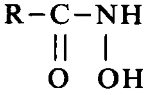
Choice of Collector

Selective extraction of zirconium from uranium in carbonate media by ion flotation depends on the choice of a suitable collector. Some work has been done with other media as indicated in Table 1 (*12–14*), but the collec-

TABLE 1
Previous Works on Zirconium Ion Flotation

Colligend	Medium	pH	Collector	Ref.
ZrF_6^{2-}	Aqueous	2-3	Dodecylamine Armeen 12 D	12
Zr(IV)	Nitric acid	1-7	Sodium lauryl sulfate	13
Zr(IV)	Oxalate	>1	Cetylpiridinium chloride	14

tors used are not efficient for such separations. In effect, the cationic collectors (amines and quaternary ammoniums) have already been used for the ion flotation of uranium in carbonate solutions (*15, 16*), and the anionic collector (sodium lauryl sulfate) does not react with zirconium in these media. Therefore, other collectors with strong complexing properties and which are known by their good selectivity in high ionic strength media were tested (*4, 17*). The best results were obtained with the octylhydroxamic acid (HOHX):



$$R-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{OH}}{NH}$$

where $R = C_8H_{17}$. This collector gives a well-flocculated precipitate with zirconium, and its affinity for this cation is higher than for uranium. In fact, precipitation of uranium occurs only when its concentration is higher than 10^{-2} *M*.

Moreover, filtration of the "uranium-collector" precipitate is difficult, whereas that obtained with zirconium is not. The physical nature of the two precipitates is therefore different. The "zirconium-collector" precipitate contains 12.3% Zr on average. This composition corresponds to a stoichiometry for HOHX/Zr of 3.9/1, which agrees with previous studies on the solvent extraction of zirconium with hydroxamic acids (*18, 19*).

In carbonate media, zirconium can form such complexes as $[ZrO(CO_3)_2]^{2-}$ and $[Zr(OH)_4(CO_3)_2]^{4-}$ (*20*), and the precipitation reactions can be written

$$[ZrO(CO_3)_2]^{2-} + 4HOHX \rightarrow Zr(OHX)_4 + 2HCO_3^- + H_2O \qquad (1)$$

and

$$[Zr(OH)_4(CO_3)_2]^{4-} + 4HOHX \rightarrow Zr(OHX)_4 + 2HC\,O^-_3 + 2OH^- + 2H_2O \quad (2)$$

However, Reaction (2) is favored because the precipitation of Zr is accompanied by an increase of the pH.

Ion Flotation of Zirconium

Tests were first run in synthetic carbonate solutions in order to study the concentration effects of collector zirconium and carbonate anions. Later, industrial carbonate media from the reextraction cycle of uranium were used.

Whatever the parameter studied, flotation tests show that for a bubbling flow rate of 2 L/h, the organometallic precipitate "Zr-collector" floats in less than 5 min and the liquid content of the froth (Lc %) is less than 10%. The Lc % is defined by the following relation:

$$\text{Lc}\ \% = \frac{\text{volume of solution in the froth}}{\text{initial volume of solution}} \times 100$$

Synthetic Media

Effect of Collector and Zirconium Concentrations. Results are given by Tables 2 and 3. It can be seen from Table 2 that the removal rate of zirconium increases with the Φ value and reaches 99% at $\Phi = 4$. For this value of Φ, equal to the stoichiometry, the removal rate obtained indicates that the reaction is very quantitative. From Table 3 it can de deduced that the removal of zirconium is not affected by the initial Zr concentration of the solution. The high removal rate obtained for a low concentration in colligend enables good selectivity to be reached in the presence of uranium.

Effect of Carbonate Concentration. Tests were run at $\Phi \approx 5.3$ and pH 7.8. As shown in Table 4, the zirconium removal rate remains constant (close to 99.8%) whatever the carbonate concentration. This is certainly due to the low stability of zirconyl carbonate complexes (*21*) and to the high affinity of hydroxamic acid for zirconium.

TABLE 2
Effect of Collector HOHX Concentration on Zr Removal in Synthetic Solutions: Zr 65.5 mg/L; Na_2CO_3 30 g/L; pH 7.8

Φ = [HOHX] / [Zr]	3	6	9	12
Removal %	78.6	99.8	99.8	99.8

TABLE 3
Effect of Zr Concentration on the Removal in Synthetic Solutions: Na_2CO_3 30 g/L; Φ = 4; pH 7.8

Initial Zr, mg/L	52.2	146.2	302.0
Removal %	99.8	99.9	99.9

TABLE 4
Effect of Carbonate Concentration on Zr Removal in Synthetic Solutions: Φ = 5.3; pH 7.8

Na_2CO_3, g/L	15	30	45	60
Initial Zr, mg/L	74.8	65.5	68.7	67.8
Removal %	99.8	99.8	99.8	99.8

Industrial Media

The industrial media are carbonate solutions of reextraction, supplied by Somair (Niger). Their characteristics are: uranium, 37.4 g/L; zirconium, 762 mg/L; Zr/U = 2.04%; pH 7.8.

The results compiled in Tables 5, 6, and 7 were obtained for zirconium removal as a function of collector concentration, pH, and temperature, respectively.

As in synthetic media, the zirconium removal rate was found to increase with the collector concentration. At a Φ ratio of 4, which is just stoichiometric, it reaches 99% (Table 5). Therefore, the precipitation reaction remains very quantitative even in the presence of a high uranium

TABLE 5

Effect of Collector Concentration on Zr Removal in Industrial Media (Somaïr): pH 7.8; 25°C

	Precipitate content (%)		Residual zirconium	Zr removal	U loss	
Φ	U	Zr	(mg/L)	(%)	(%)	Zr/U (%)
2	1.84	11.52	336.0	52.3	0.2	0.96
4	2.33	10.56	006.4	99.0	0.5	0.02
6	4.19	08.84	005.7	99.0	1.0	0.02

TABLE 6

Effect of pH on Zr Removal in Industrial Media (Somaïr): Φ = 4; 25°C

pH	Residual Zr (mg/L)	Zr removal (%)	Zr/U (%)
7.8	7	98.9	0.020
5.9	7	98.9	0.022
9.8	8	98.9	0.024

TABLE 7

Effect of Temperature on Zr Removal in Industrial Media (Somaïr): Φ = 4; pH 7.8

T (°C)	Residual Zr (mg/L)	Zr removal (%)	Zr/U (%)
25	8	98.7	0.024
40	8	98.7	0.024
60	8	98.7	0.024

concentration. Still, when Φ is increased, the zirconium content of th precipitate decreases whereas its uranium content grows. Then the loss of uranium becomes more important, but for Φ = 4 it remains at an acceptable level of 0.5%, comparable to that obtained by other zirconium removal processes such as hydrolysis.

In the range of pH and temperature studied, the elimination of Zr is not affected by these two parameters (Tables 6 and 7). However, there is a change in the precipitate color at pH 5.9, probably due to a more important interference by uranium.

According to the above results, Φ = 4 enables the Zr content of industrial solutions to be reduced to a level of Zr/U ≈ 0.02%. At this consumption of collector, the loss of uranium is low.

CONCLUSION

In light of the results obtained, the selective removal of zirconium contained in industrial carbonate solutions from uranium can be easily achieved by ion flotation by using octylhydroxamic acid as the collector.

The interaction of zirconium and the collector is very strong and is certainly by chelation, which enables the formation of a well-flocculated precipitate with hydrophobic properties. In fact, it is possible to collect all of this precipitate in the foam in less than 5 min with a liquid content not exceeding 10% of the initial volume of the solution in the froth.

Interference by uranium is very low, which leads to a loss of only 0.5% for a value of Φ = 4, although the initial concentration of the solution was 37.4 g/L in uranium. Therefore, this interference will be negligible in leaching carbonate solutions where the uranium content is less than 3 g/L.

The Zr/U ratio of the solution can be reduced from 2.04 to 0.02%. This value, though slightly higher than the penalty limit according to ASTM norms, will not be penalized by some companies which specialize in the conversion of uraniferous concentrates and which accept Zr/U ratios up to 0.2%.

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