

Technical note

Uranium stripping from tertiary amine by sulfuric acid solution and its precipitation as uranium peroxide

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Abstract

The uranium stripping results from a loaded tertiary amine (Alamine[®]336) by sulfuric acid solution and the uranium peroxide precipitation from the pregnant strip solution (PSS) are presented. The following steps were investigated: (i) uranium stripping; (ii) sulfate content reduction from the PSS and (iii) uranium peroxide precipitation. The experiments were carried out in batch as well as in continuous scale. In the stripping stage, a PSS containing 96 g/L of U₃O₈ was obtained, using a 4.0 mol/L H₂SO₄ stripping solution in six mixer-settler stages. The sulfate content reduction from the PSS was carried out by the addition of lime up to pH 3.0. After sulfate excess removal, uranium precipitation was carried out by H₂O₂ and MgO/Mg(OH)₂ powder addition. A calcining product assaying 99.7% U₃O₈ was obtained.

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1. Introduction

Uranium concentrate production in Brazil is under Indústrias Nucleares do Brasil SA (INB) responsibility. The INB mining and milling facilities, called Uranium Concentrate Plant (UCP), is located in the neighborhood of Caetité city, Bahia State.

In the UCP process, the uranium stripping is carried out by sodium chloride (NaCl) solution, and all aqueous effluent is recirculated after lime treatment up to pH 9. As the chloride ion is not removed in this treatment, its content in the liquor has increased, causing a drop in the uranium extraction efficiency.

This study intended to replace the NaCl solution used in the UCP uranium stripping step. For that, the uranium stripping from a loaded Alamine[®]336 solution by sulfuric

acid and its precipitation as uranium peroxide from the pregnant strip solution (PSS) was investigated. Stripping studies were carried out in batch as well as in continuous scale. Before the uranium peroxide precipitation study, the sulfate content reduction was carried out through its precipitation as hydrated calcium sulfate (CaSO₄·xH₂O) by adding lime milk. Uranium peroxide precipitation experiments were carried out by hydrogen peroxide (H₂O₂) addition and reaction pH control by the addition of magnesium oxide/magnesium hydroxide (MgO/Mg(OH)₂) mixture.

2. Experimental

2.1. Reagents and solutions

The loaded organic solution containing 8.0 g/L U₃O₈, 2.3 g/L Cl⁻ and 10.5 g/L SO₄²⁻ was supplied by INB/UCP. It consists of 0.15 mol/L Alamine[®]336 and 3% v/v tridecyl alcohol, used as modifier, and purified kerosene, used as diluent. Both Alamine[®]336 and tridecyl alcohol

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were supplied by “Cognis do Brasil Ltda”. Purified kerosene (Solbrax ECO[®]175/235) was supplied by “Petrobrás Distribuidora S/A”. All other reagents used were of analytical grade and their respective solutions were prepared with distilled water.

3. Experimental procedure

The batch experiments of uranium stripping, sulfate content reduction from the PSS and uranium peroxide precipitation were all carried out in beakers under mechanical agitation at room temperature (24–27 °C). An organic and aqueous phase ratio (O/A) equal to 1 was used in all stripping experiments. The sulfate content reduction and the uranium peroxide precipitation were carried out under controlled pH and precipitation time of 3 h.

The continuous stripping experiments were carried out in a countercurrent system using polycarbonate mixer-settlers cells, with mixers of 300 cm³ and settlers of 1000 cm³ capacity. The experiments were controlled by sampling and analyzing the effluent flows from both aqueous and organic phases.

4. Results and discussion

4.1. Batch experiment

The H₂SO₄ concentration effect on uranium stripping was investigated in the range of 2.0–5.0 mol/L. In this range the uranium stripping efficiency increases from 24% to 75%, indicating that the uranium stripping from loaded Alamine[®]336 by H₂SO₄ has to be done in high acid concentration.

The results obtained indicated that the increase on uranium stripping distribution coefficient reduces significantly above 3.5 mol/L H₂SO₄ concentration. Contact time between phases was investigated between the interval of 3 and 10 min. It was observed that 5 min were enough to achieve the metal equilibrium between the phases. The stripping isotherm/McCabe–Thiele diagram (Ritcey and Ashbrook, 1984) to estimate the theoretical stages number and the volumetric ratio of organic and aqueous phases feeding to be used in the continuous experiments was carried out using 4.0 mol/L H₂SO₄ with 5 min contact time. The McCabe–Thiele diagram indicates that about six mixer-settler stages are required to achieve a PSS containing about 100 g/L U₃O₈ and a barren solvent (Fig. 1).

4.2. Continuous experiment

The continuous experiment was carried out using 4 mol/L H₂SO₄ solution as stripping agent in six mixer-settler stages. The volumetric ratio between organic and aqueous phases (O/A) feeding was 12, aiming at obtaining a PSS of 96 g/L U₃O₈. After 30 h of experiment, a pregnant strip solution containing 96.3 g/L U₃O₈ was obtained. The

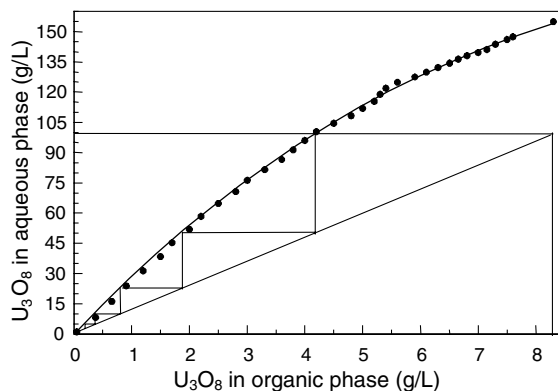


Fig. 1. McCabe–Thiele diagram for a stripping solution load of 100 g/L U₃O₈.

uranium content in the organic phase in the fifth and sixth stages was 70 and 28 µg/mL U₃O₈, respectively.

4.3. Sulfate content reduction

In order to reduce the sulfate content to avoid final product contamination before the uranium peroxide (UO₄ · xH₂O) precipitation, the sulfate precipitation as CaSO₄ from the PSS was investigated. Sulfate was removed by adding aqueous lime milk. The influence of the reaction pH on CaSO₄ precipitation by evaluating the uranium content in the precipitate, and the sulfate content in the filtrate was investigated in the range of pH 1.0–4.0. The initial sulfate content in the uranium PSS was 311 g/L SO₄²⁻. The results of these experiments are presented in Table 1.

One can see that uranium content in precipitate increases significantly as the CaSO₄ precipitation pH increases from 3.0 to 4.0, while for the 1.0–3.0 pH interval this variation is negligible. Sulfate content in filtrate decreases as pH increases, but there is no significant difference between pH 2.0 and 4.0. pH 3.0 was chosen for the sulfate reduction content.

4.4. Uranium peroxide precipitation

The literature of uranium peroxide precipitation suggests a reaction pH range of 2.5–4.0 (Merritt, 1971) or of 3.4–5.0 (Shabbir and Tame, 1974). Gupta et al. (2004), working with 3.8 g/L U₃O₈ iron-free eluted solution, suggested the uranium peroxide precipitation time of 4 h at a final pH of 3.5. In all of these cases, the pH values were obtained by adjustment with NH₄OH solution. In the present work, it was observed that 3 h were enough for the full

Table 1
Influence of the reaction pH on CaSO₄ precipitation

	pH			
	1.0	2.0	3.0	4.0
U ₃ O ₈ in precipitate (µg/g)	400	430	520	1900
SO ₄ ²⁻ in filtrate (g/L)	16.2	11.1	8.9	6.8

uranium precipitation. The reaction pH was maintained between 2.8 and 3.0 by adding a mixture of MgO and Mg(OH)₂ powder.

The H₂O₂ excess on the uranium peroxide precipitation was based on the following reaction:



According to Eq. (1), 0.126 kg of H₂O₂ is required for each kilogram of UO₂. It is known, however, that excess hydrogen peroxide is necessary. This excess may vary according to the uranium solution composition (Shabbir and Tame, 1974). In this work, the H₂O₂ excess investigation on UO₄·2H₂O precipitation indicated that an excess of 30% H₂O₂ is required for full uranium precipitation. After a precipitation time of 3 h at room temperature and using a 30% H₂O₂ excess, a filtrate with 1 µg/mL was obtained. The calcined UO₄·2H₂O at 800 °C assayed 99.7% U₃O₈.

5. Conclusions

The major advantage of uranium stripping from loaded Alamine[®]336 by H₂SO₄ solution is the loading power of

the stripping solution, which can exceed 100 g/L U₃O₈. Optimal pH for partial sulfate removal is between 2 and 3. At this pH range, there is a low uranium co-precipitation and the sulfate removal is quite efficient. Uranium peroxide precipitation from the pregnant strip solution after sulfate content reduction seems to be a good option. Under a reaction at pH 3.0 and 30% H₂O₂ excess, a high uranium precipitation output and a high purity uranium peroxide (99.7% U₃O₈) were obtained.

References

- Gupta, R., Pandey, V.M., Pranesh, S.R., Chakravarty, A.B., 2004. Study of an improved technique for precipitation of uranium from eluted solution. *Hydrometallurgy* 71, 429–434.
- Merritt, R.C., 1971. *The Extractive Metallurgy of Uranium*. Colorado School of Mines Research Institute, Colorado.
- Ritcey, G.M., Ashbrook, A.W., 1984. *Solvent Extraction. Principles and Applications to Process Metallurgy—Part 1*. Elsevier, Amsterdam.
- Shabbir, M., Tame, K.E., 1974. Hydrogen peroxide precipitation of uranium. US Bureau of Mines, USA, RI 7931.