

Uranium stripping from loaded synergic solvent by sodium carbonate using pulsed column

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ABSTRACT

The uranium stripping results from a loaded synergic solvent (3%D2EHPA/3% TBP) by sodium carbonate solution and the uranium peroxide precipitation from the pregnant strip solution (PSS) are presented. The experiments were carried out in batch as well as in continuous scale (laboratory pulsed column). In a laboratory pulsed column, operating parameters have been optimized as 0.036m/s pulsation intensity and 30m/hr flux (total flowrate), through hold-up and uranium stripping efficiency measurements. Thereafter PSS containing 48gU/l was obtained, the sulfate content reduction from the PSS was carried out by the addition of lime up to pH 3.0 then; uranium precipitation was carried out by H₂O₂ addition. A calcining product assaying 80.33% U was obtained.

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KEYWORDS

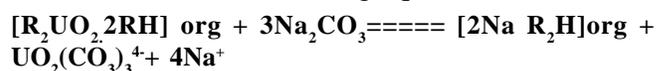
Uranium stripping;
D2EHPA/TBP synergic
solvent;
Na₂CO₃ and H₂O₂.

INTRODUCTION

For uranium stripping from the scrubbed uranium-loaded mixed Amex solvent (3%D2EHPA/3%TBP), several reagents could be employed, viz: such as ammonium sulfate/ammonia, sulfuric acid, sodium carbonate, and sodium chloride, indeed the most common stripping medium in such a system is ammonium sulfate together with ammonia (gas or aqueous solution) being used for pH control during stripping. However, environmental and transport considerations associated with the use of ammonia have recently sparked the interest in alternative stripping reagents. Stripping with ammonium sulfate should be a reasonably attractive option for most applications except in areas where dumping of NaCl would be acceptable (saline ground water). The recycling

of ammonia via lime boiling might become an increasingly attractive option for ammonium sulfate stripping. In the meantime, while sulfuric acid could be considered as an effective stripping agent, however the recovery efficiency of the sulfuric acid prior to uranium precipitation would be critical. From the above giving's, it was decided to apply the Na₂CO₃ option which would produce a relatively small waste stream in spite of the mass of waste production is large^[1,2].

The stripping mechanism by sodium carbonate is illustrated in the following equation;



The carbonate strip would completely deprotonates the organic mine extractant and all the extracted anions would report to the strip

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aqueous phase. The final pH of such solution could be around 7.3 (pKa value for $\text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$ is 6.3). The solubilities of Na_2CO_3 and NaHCO_3 are 210 g/L (2 M) and 100 g/L (1.2 M) at 20°C respectively. Hence, if the feed concentration of Na_2CO_3 is higher than 1.2 M (130 g/L Na_2CO_3), precipitation of NaHCO_3 might occur in the mixer/settler if no pH control is done via NaOH addition and a maximum organic-to-aqueous (O:A) phase ratio is targeted. Stripping of uranium from the scrubbed loaded solvent was achieved by its shaking with 120 gm Na_2CO_3 [1,2].

The mass transfer between the flowing liquid phases in an extraction column depends, among other factors, on the contact interfacial area between continuous and dispersed phases. The interfacial area available for mass transfer in a counter-current extraction tower depends upon the volume fraction or holdup, of the dispersed phase, as well as on the mean droplet size. In addition, a set of correlations have been developed for standard internals to predict maximum flux (V_{max}) and pulsation intensity ($f.a$) = amplitude * frequency at maximum flux and, for a given phase ratio and with the desired phase continuity – organic or aqueous. Maximum flux was selected and correlated using Equation 1:

$$\text{MaxFlux} = (V_c + V_d)_m = (24,528 + 2,537 \sigma + 0,0548 \sigma^2)(1 + 1,455\alpha + 3,247 \alpha^2)(1 + 0,1788 \ln(V_c/V_d) + 0,0437 \{\ln(V_c/V_d)\}^2) \quad (1)$$

Simple models of pulsation intensity was suggested for the transition from the mixer-settler to the dispersion (boundary) and from the dispersion to the emulsion regime in perforated-plate pulsed col-

umns as in the following correlation [3].

$$\text{From m.s to d } (f.a)_{m/d} = 9.69 \cdot 10^{-3} (\sigma \Delta \rho^{0.25} \alpha / \mu_d^{0.75})^{0.33}$$

$$\text{From d to em } (f.a)_{d/em} = 0.5 \sqrt[3]{0.96 \cdot \alpha^2 / \rho_c} \quad (\text{m/s}) \quad (2)$$

Dispersed phase holdup which defined as the fraction of the active column section volume occupied by the dispersed phase was correlated in a series of articles, based on more than 2000 experimental points, for perforated-plate pulsed columns [4]. The holdup correlated directly from the physical data, energy input and flow rates, avoiding the problematic concept of characteristic velocity. The fit of their work was quite good – average deviation of 13%.

$$X_d = k_1 \exp [k_2 ((f.a) - (f.a)_m)] V_d^{0.86} (V_c + V_d)^{0.28} \mu_d^{0.77} \Delta \rho^{-0.3} \rho_d^{0.93} h^{-0.56} \alpha^{-0.56} \quad (3)$$

The value of k_1 varies from $1.1 \cdot 10^6$ for mass-transfer from the dispersed to continuous phase to $2.14 \cdot 10^6$ for the continuous to the dispersed one. The values of k_2 are 50.26 and 44.53, accordingly.

EXPERIMENTAL

Reagents and solutions

The loaded organic solution containing 3.9 gU/L, 0.07 g/L Cl_- and 0.18 g/L Fe was supplied by extraction of uranium eluate produced in Gattar mini pilot plant. It consists of 3% v/v. tri-butyl phosphate, 2% D2EHPA and purified kerosene, used as diluent. Both tri-butyl phosphate, D2EHPA were supplied by “Cognis do Brasil Ltda”. Purified kerosene (Solbrax ECO) was supplied by “Petrobra’s S/A”. All other reagents used were of analytical grade and their respective solutions were prepared with distilled water.

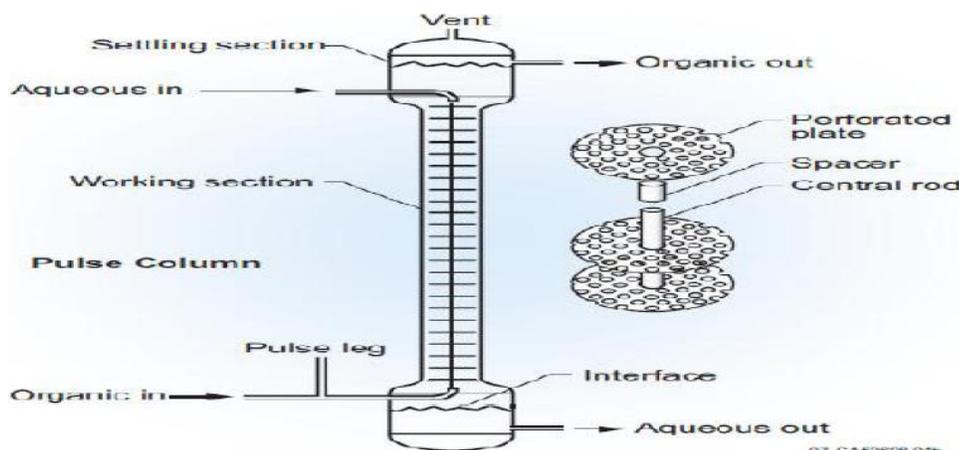


Figure 1 : Sketch of pulsed perforated plates column

Experimental procedure

The batch experiments of uranium stripping and uranium peroxide precipitation were all carried out in beakers under mechanical agitation at room temperature (25–30°C). The uranium peroxide precipitation was carried out under controlled pH and precipitation time of 3 h.

The continuous stripping experiments were carried out in a countercurrent system using in a pulsed perforated-plate extraction column of 120 mm long with diameter of 50 mm, enclosing a stack of sieve plates. Below the plate section was a 120mm expanded glass section enclosing a PVC solvent distributor supported on a piston-type pulsing unit, which imparted a sinusoidal motion to the fluids of the column. In total, 20PVC sieve plates were arranged alternately and spaced 50 mm apart in the column. They had a 2mm perforation diameter and 22.7% free area. The inlets and outlets of the column were connected to four tanks, each of 5 liters capacity. All that are illustrated in Figure (1). The experiments were controlled by sampling and analyzing the effluent flows from both aqueous and organic phases out let.

RESULTS AND DISCUSSION

Batch experiment

By applying the studied optimum extraction conditions on a prepared uranium standard solution assaying 7gU/l, it was found that the obtained saturation capacity of the working mixed Dapex solvent (3%D2EHPA/3%TBP) has attained 5.45g U/l while that by the working eluate has attained 4.15 g U/l. Thus, it can be mentioned that the difference of 1.3g

must have been occupied by the equivalence of other impurities and hydrogen ions. Before the uranium stripping from a prepared loaded solvent assaying 4.1g U/l, a scrubbing step was performed for reducing the concentration of the co-extracted impurities. For this purpose, 0.5 M H₂SO₄ acid solution was used as a scrubbing agent at an O/A ratio of 1/1 through a single contact (Brooy, et al,2009, Vahidi, et al,2010) and for minute and where the assay of the scrubbed uranium and iron in such solution was found as 0.05 and 0.55 g/l respectively and accordingly, the uranium assay in the scrubbed loaded solvent has decreased to 4.05g U/l.

Using 120g Na₂CO₃/l, the other stripping factors were studied; namely, the contact time, the stripping temperature and the O/A ratios in the manner to construct the McCabe-Thiele stripping diagram.

Effect of contact time

Five aliquot portions of the prepared 120 g/l Na₂CO₃ stripping solution were shaken with the prepared scrubbed loaded organic solvent (4.05 g-U/l) in an O/A ratio OF at room temperature for different contact time periods (0.5 to 4 min). The obtained results tabulated in TABLE (1) and represented in Figure (2) show that an almost complete uranium stripping (97%) was achieved during the first minute and has attained almost complete stripping (99.9%) at 2 minutes.

Effect of temperature

The temperature effect upon uranium stripping by Na₂CO₃ solution from the scrubbed loaded solvent (4.05 g-U/l) was studied in the range of room to 60°C by shaking five aliquot portions of the latter with the prepared 120gNa₂CO₃/l solution in an O/A

TABLE 1 : Effect of contact time on uranium stripping efficiency from scrubbed loaded 3%D2EHPA/3%TBP mixed solvent in kerosene using 120g Na₂CO₃/l solution

Contact Time(min)	U assay at equilibrium,g/l		D ^a U	%U stripped
	Aq phase	Org phase		
0.5	3.18	0.87	3.65	78.5
1	3.92	0.13	30.15	97.0
2	4.045	0.005	809	99.9
3	4.045	0.005	809	99.9
4	4.045	0.005	809	99.9

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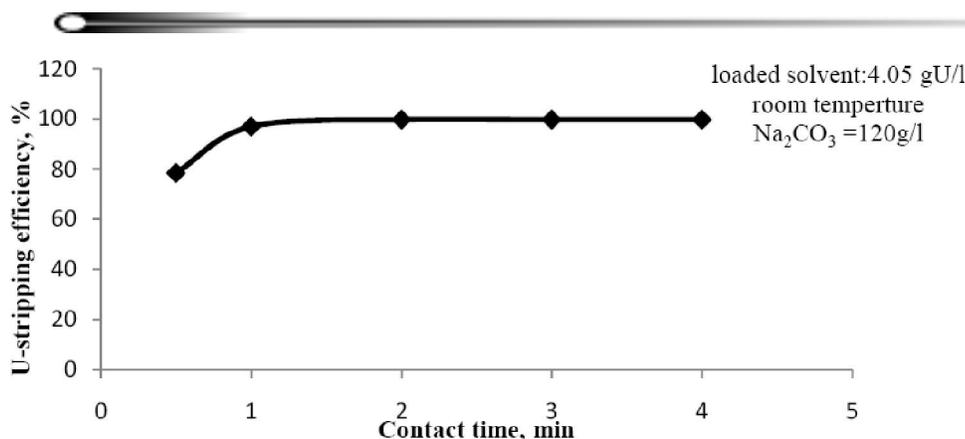


Figure 2 : Effect of contact time on uranium stripping efficiency from the scrubbed loaded D2EHPA/TBP mixed solvent in kerosene using 120g Na₂CO₃/l solution

TABLE 2 : Effect of temperature on uranium stripping efficiency from the scrubbed loaded 3% D2EHPA/3% TBP mixed solvent in kerosene using 120g Na₂CO₃/l solution

Temperature, °C	U assay at equilibrium, g/l		D ^a , U	% U stripped
	Aq phase	Org phase		
25	4.05	0.005	809.00	99.9
30	4.05	0.005	809.00	99.9
40	4.00	0.05	80.00	98.8
50	3.65	0.40	9.13	90.1
60	2.80	1.25	2.24	69.1

ratio of 1/1 for 2 minutes. The obtained results are summarized in TABLE (2) and plotted in Figure 3.

From the obtained results, it was appeared that increase of the temperature behind 40°C is actually associated with a gradual decrease in the uranium stripping efficiency down to 90.1 and 69.1% at 50 and 60°C respectively. This can be attributed to the degradation effects of the working 3% D2EHPA/3% TBP mixed solvent; a matter which indicates that room temperature would be considered as the optimum for uranium stripping from the working mixed solvent.

Effect of O/A ratio and construction of the McCabe-thiele stripping diagram.

The stripping equilibrium isotherm of the working system was determined by contacting the uranium-loaded solvent after scrubbing with the working aqueous strip solution using a magnetic stirrer at different O/A phase ratios varying from 2 to 20 at ambient temperature for 5 minutes. The obtained results are summarized in TABLE (3) and the corresponding equilibrium isotherm is plotted in Figure (4). To the latter, a proper operating line was fitted

and whose slope defining the O/A flow rate of about 15 would result in 2 theoretical stripping stages. On the other hand, the uranium concentration in the resultant strip solution would attain up to about 63g/l.

Continuous experiments

The resulted uranium loaded solvents from first continuous stage were collected and go on second stage to be saturated by uranium then its physical properties were measured in Pet. Inst. Of Egypt, then operating conditions were calculating using mentioned correlations above from which. All results were tabulated in TABLE (4,5).

From TABLE (5), it's obvious that; (a) low interfacial tension of two liquids which mean low interfacial area between to immiscible liquids which lead to the necessity of higher driving power for completing uranium stripping., (b) The large density difference makes the loaded solvent to be dispersed phase and 120g Na₂CO₃ be continuous one., (c) High value of O/A ratio; which play important role in mass transfer since, a higher value of (V_d/V_c) may cause large backmixing. Accordingly, bad performance is obtained in both cases and intermediate ratio must

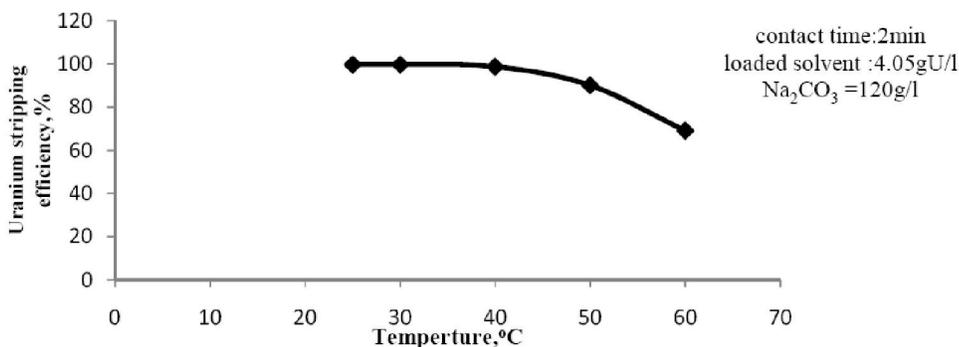


Figure 3 : Effect of temperature on uranium stripping efficiency from the scrubbed loaded 3%D2EHPA/3%TBP mixed solvent in kerosene using 120g Na₂CO₃/l solution

TABLE 3 : Effect of O/A-ratio on uranium stripping from scrubbed loaded 3%D2EHPA/3%TBP mixed solvent in kerosene using 120g Na₂CO₃/l solutions

O/A ratio	U assay at equilibrium, g/l	
	Aq- phase	Org-phase
2	8.10	0.00
4	16.20	0.00
6	24.30	0.00
8	32.00	0.05
10	40.00	0.05
12	47.88	0.06
14	55.16	0.11
16	60.80	0.25
18	62.10	0.60
20	63.40	0.88

therefore be chosen. On the contrary, low value of dispersed to continuous phases (V_d/V_c) is manifested in the reduction of the dispersed phase hold up and hence the reduction of the interfacial area.^[4,5,6] There is no positive control of the O/A ratio within the mixing region of the column. The mixerregion O/A ratio and the phase continuity is supposedly determined by the organic hold up volume^[7]. However there is no positive way to either measure this hold up or to control it. Adjustment of the column pulse and stroke may offer some degree of control but this control is neither positive nor linear. It is also uncertain as to whether the O/A ratio is constant over the height of the column^[8]. There are examples where the use of columns in pilot plant stripping and scrubbing operations has met with difficulties. The back mixing effect is significant when the phase ratio is above O:A= 10[v/v]^[9], (d) The highest O/A ratio will lead to the slower velocity of continuous phase, consequently the column performance (volumetric

mass transfer coefficient) will be decrease^[10].

Optimizing parameters of a sieve plate pulsed column for uranium stripping

Calculated parameters in TABLE (5) will be used as guidelines to determine the range of pulsation intensity and maximum flux to be studied for uranium stripping from loaded solvent 3% TOA+2%D2EHPA by using 120g Na₂CO₃ solution. Stripping process will be performed using pervious obtained O/A ratio of each and maximum reached frequency. At steady state of process the holdup and uranium in raffinate will be determined and tabulated in TABLE (6). From that several figures will be generated. The previous column testes supplied as the most accurate values of operating conditions for stripping. Since give the maximum stripping efficiency 82.65% at 0.036 pulsation intensity and 30m/hr flux. It's noted that the deviation between the theoretical and experimental holdup is very narrow which indicate the

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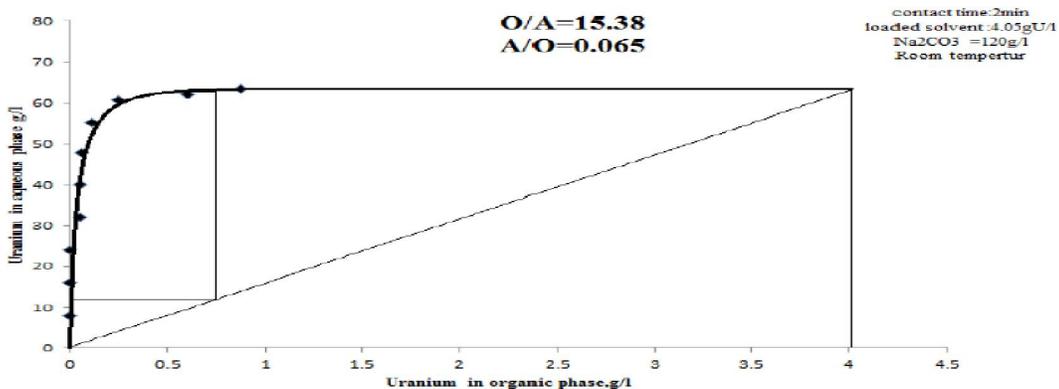


Figure 4 : Mc-Cabe Thiele stripping diagram for uranium from the scrubbed loaded mixed solvent (D2EHPA/TBP) using 120g $\text{Na}_2\text{CO}_3/\text{l}$ solutions

TABLE 4 : Physical properties of operated solutions

Physical Property	3%D2EHPA+3%TBP (loaded)-120g Na_2CO_3
$\rho_c(\text{kg}/\text{m}^3)$	1098
$\rho_d(\text{kg}/\text{m}^3)$	786
$\mu_c(\text{kg}/\text{ms}) * 10^{-3}$	1.075
$\mu_d(\text{kg}/\text{ms}) * 10^{-3}$	1.54
$\sigma(\text{mN}/\text{m}) * 10^{-3}$	3.5 \pm 0.2

TABLE 5 : Calculated theoretical operating parameters of stripping process in perforated pulsed column

Operating parameters	3%D2EHPA/3%TBP (loaded)-120g Na_2CO_3
A/O ratio	30.77
O/A ratio	0.0129
$f.a_m(\text{ms-ds})(\text{m}/\text{s})$	0.0178
$f.a_m(\text{ds-em})(\text{m}/\text{s})$	0.1358
Max flux ($\text{m}^3/\text{hr}/\text{m}^2$)	0.174
$x_d(\text{ms-ds})$	0.472
$x_d(\text{ds-em})$	30.77
$X_d(\text{max holdup at flooding})$	0.0129

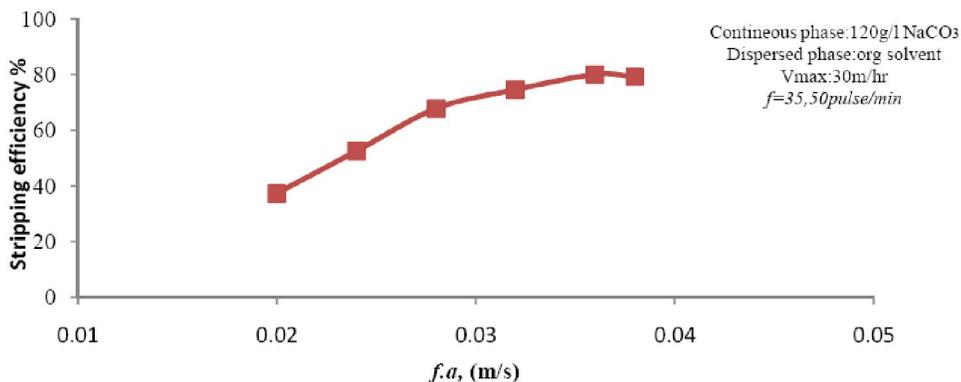


Figure 5 : Effect of pulsation intensity on uranium stripping efficiency in pulsed column

good performance of the constructed column.

Uranium precipitation

The literature of uranium peroxide precipitation

suggests a reaction pH range of 2.5–4.0^[11] or of 3.4–5.0^[12], working with 3.8 g/L U_3O_8 iron-free eluted solution, suggested the uranium peroxide precipitation time of 4 h at a final pH of 3.5. In all of these

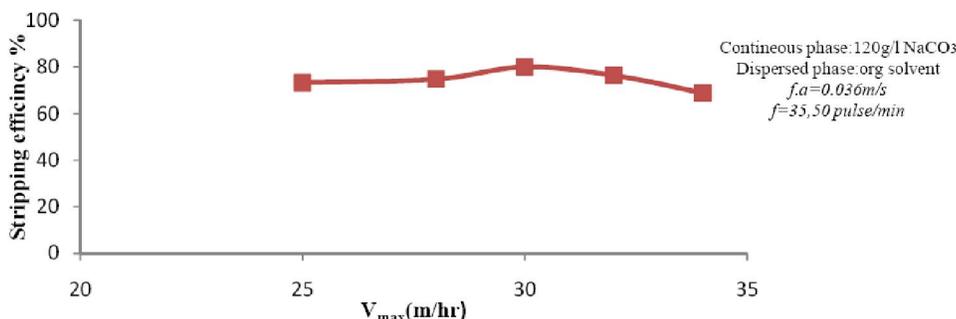


Figure 6 : Effect of flux on uranium stripping efficiency in pulsed column

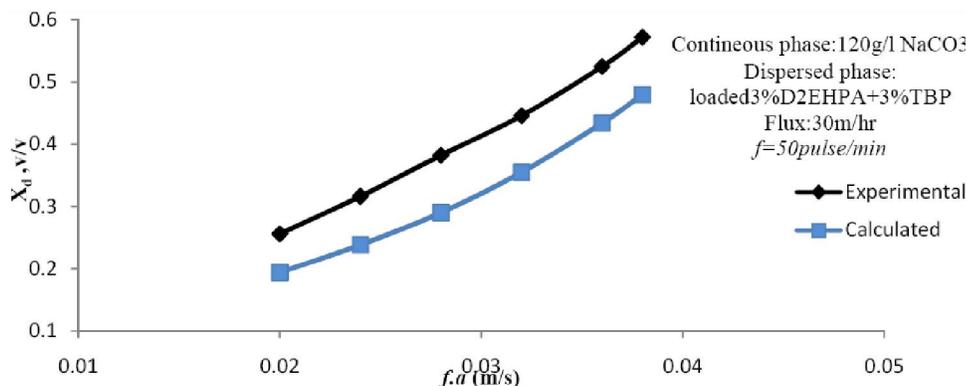


Figure 7 : Effect of pulsation intensity on holdup during stripping in pulsed column

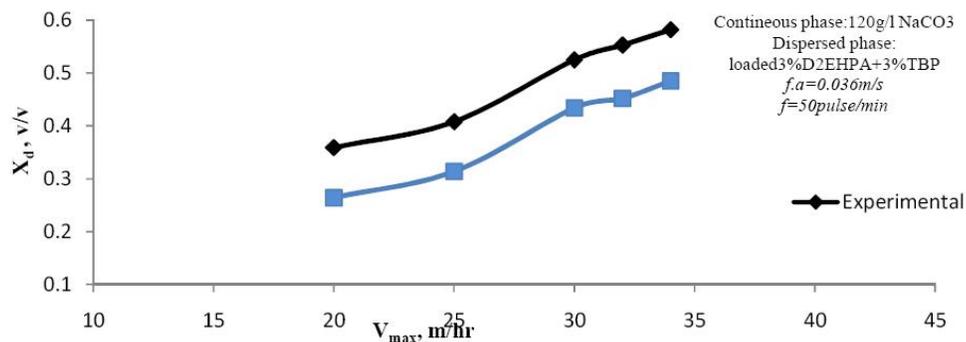


Figure 8 : Effect of flux on holdup during stripping in pulsed column

cases, the pH values were obtained by adjustment with NH_4OH solution. In the present work, it was observed that 3 h were enough for the full uranium precipitation. The reaction pH was maintained between 2.8 and 3.5 by adding NH_4OH after expel all dissolved carbonate by adding dil- H_2SO_4 at $\text{pH}=2.5$. The H_2O_2 excess on the uranium peroxide precipitation was based on the following reaction: $\text{UO}_2^{+2} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{UO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}^+$ (2)

According to Eq.^[2], 0.126 kg of H_2O_2 is required for each kilogram of UO_2 . It is known, however, that excess hydrogen peroxide is necessary. This excess may vary according to the uranium solution composition^[13]. In this work, the H_2O_2 excess investigation

on $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ precipitation indicated that an excess of 30% H_2O_2 is required for full uranium precipitation. After a precipitation time of 3 h at room temperature and using a 30% H_2O_2 excess, a filtrate with 1 $\mu\text{g}/\text{ml}$ was obtained. The calcined $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ at 380°C assayed 81.54 % U.

CONCLUSIONS

The major advantage of uranium stripping from loaded synergic mixture D2EHPA/TBP by Na_2CO_3 solution is the loading power of the stripping solution, which can exceed 60gU/L. In spite of the difficulty and slow kinetics of stripping process to be

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applied in pulsed column but also give good results and show the feasibility of working and ease of construction in the field than in mixer settler one. 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% H_2O_2 excess, a high uranium precipitation output and high purity uranium peroxide (80.33% U) were obtained at calcination at 380°C.

NOMENCLATURE

V_c, V_d are Continuous and Dispersed flow per unit of time and cross section area [m/h],

Pulsation Intensity ($f.a$)=Amplitude*Frequency, m/s or mm/min,

σ - Interfacial tension [10^{-3} N/m],

α - Free fractional plate area,

x_d - Dispersed phase holdup fraction,

h - Compartment height (m),

d - Inner diameter of the column (m), d_0 : Plate hole diameter,

μ_c - Continuous phase viscosity, μ_d : Dispersed phase viscosity,

h : Center-to-center plate spacing*:Standard plate spacing=0.05m,

ρ Density, ρ^* -Density of water at 20°C=998 kg/m³, $\Delta\rho$ -Density difference between phases.

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