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STUDY OF THE INER PROCESS FOR URANIUM RECOVERY FROM WET-PROCESS PHOSPHORIC ACID

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ABSTRACT

The effects of process parameters on the performance of the INER process for recovery of uranium from wet-process phosphoric acid were studied via pseudo dynamic simulation technique. The process parameters investigated include the organic-to-aqueous flow ratio, the aqueous feed-to-stripping agent flow ratio, stage configuration and flow arrangement. The flow arrangements concerned include countercurrent, crosscurrent, and alternating extraction and stripping. The calculated results are in good agreement with the pilot plant data. An improvement of the process performance based on simulation results was also proposed.

INTRODUCTION

Uranium is an important nuclear resource which has been providing the most energy needed today. Besides in natural uranium ore, this valuable nuclear fuel material also resides in natural phosphate rock in huge amounts with a very low content(1,2). Since the operation of the first plant for recovery of uranium from phosphoric acid in 1950, various chemical processes have been developed and many commercial scale plants have been constructed to recover uranium from phosphate rocks directly or from wet-process phosphoric acid(3). The Institute of Nuclear Energy Research (INER) of the Chinese Atomic Energy Council began considering development

of a process for recovering the uranium from the wet-process phosphoric acid of the China Phosphate Co., Ltd.(now the China Petrochemical Development Corp.) in 1977. Based on the laboratory results, a pilot plant was constructed in 1979 to confirm the process conditions. Since started-up in May/1981, a full scale production plant has been successfully operated for more than six years. The INER process(3-6) was based on the liquid-liquid solvent extraction technique with di-(2-ethylhexyl)-phosphoric acid(D2EHPA) and tri-octyl phosphine oxide(TOPO) in kerosene as the organic phase. This process was mainly composed of two extraction and concentration cycles and an ammonium precipitation step. A countercurrent flow pattern was adopted in the extraction and stripping cascades.

It has been thought for quite a long time that a countercurrent flow arrangement between two immiscible streams will privide the most effective concentration difference for mass transfer. But recently, Rod(7) found that a crosscurrent flow arrangement is more efficient than a countercurrent flow arrangement for copper extraction with hydroxyoximes, and Li(8) found that an alternating extraction and stripping flow arrangement is also more efficient than a countercurrent flow arrangement for the iron extraction with n,n-di-(1-methyl)-acetyl amide(N503) and the phosphoric acid extraction with dibutyl sulfoxide(DBSO). A simulative comparison among those three flow arrangements made by Ju et al.(9) indicated that the crosscurrent flow arrangement is superior to the other two arrangements for solvent extraction processes.

One of the purposes of this work is to make a detailed study by simulation on the INER process to see what effects will result from varying process parameters, such as the organic-to-aqueous flow rate ratio(O/A) and the aqueous feed-to-stripping agent flow rate ratio(A/A'). The other purpose is to compare the results of those three flow arrangements for the INER process. The work is focused on the performance of the first cycle only because it determines the INER process performance.

MATHEMATICAL FORMULATIONS OF THE PROCESS

Process Description

A schematic representation of the INER process is shown in Fig. 1. This process involves five sections: (a) pretreatment, to remove suspended gypsum particles and humus; (b) two uranium extraction and stripping cycles, to concentrate uranium by a factor of about 134; (c) uranium precipitation, to precipitate uranium as an ammonium-uranium-tricarbonate(AUT) compound; (d) calcination, to obtain uranium as U_3O_8; (e) posttreatment, to remove the entrained solvent before returning the acid raffinate to the acid plant. The function of the first uranium extraction and stripping cycle is to concentrate the uranium content, and hence a A/A' ratio of about

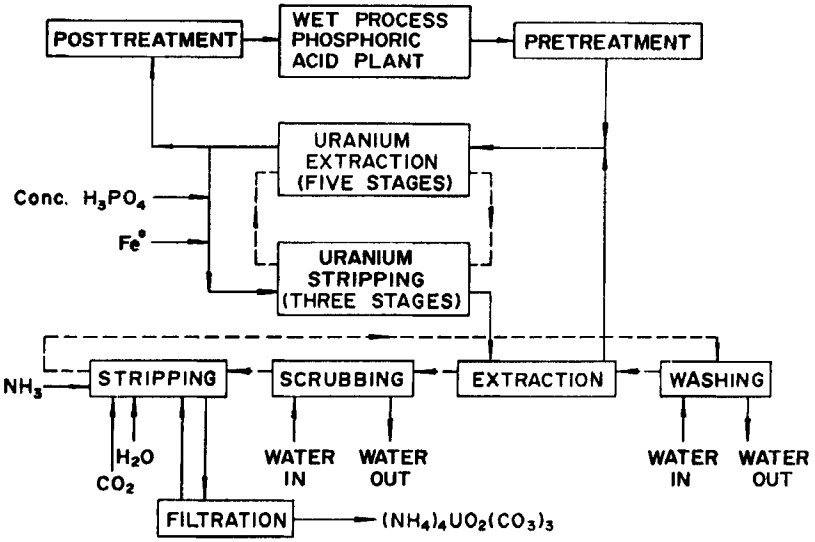

Fig. 1. Flow diagram of the INER process

134 was selected. The pilot plant has five stages for extraction and three stages for stripping in the first cycle. The production plant, however, has six stages for extraction in the first cycle.

The O/A ratio in the extraction cascade was 0.25 and that in the stripping cascade was 33.3. A conventional countercurrent flow arrangement between the organic and the aqueous streams was used. The concentration of the extractant used in this cycle was 0.5 M D2EHPA + 0.125 M TOPO in kerosene. The process conditions used in the pilot plant are listed in Table I. A detailed description of the process can be found in the patent(4).

Equilibrium Equation

The distribution coefficient for uranium with D2EHPA + TOPO in kerosene as the extractant is a function of extractant concentration, phosphoric acid concentration, iron ion concentration, temperature, etc. The equilibrium equation at low uranium concentration can be expressed as follows(10):

$$Y^* = D\,X^* \qquad (1)$$

where Y^* and X^* are the equilibrium concentrations of uranium in the organic and the aqueous phases, respectively, and D is the

Table I Operating conditions for the INER pilot plant

X_{in}	X'_{in}	(O/A)	(O/A')	(A/A')	D_{ex}
75 ppm	$=X_N$	0.25	33.3	133.3	13.9
D_{st}	E_{ex}	E_{st}	N	M	
0.0145	0.9	0.9	5	3	

Capacity: A = 1 m^3/hr
Organic phase: 0.5 M D2EHPA + 0.125 M TOPO in Kerosene

distribution coefficient, which is a function of temperature, phosphoric acid concentration, extractant concentration, etc.. The values of the distribution coefficient associated with the pilot plant operating conditions are also given in Table I.

Flow Arrangement

Varieties of flow arrangements between the aqueous and organic streams can be easily conceived for a certain solvent extraction process. Figs. 2a to 2c show three different flow arrangements.

The countercurrent(CTC) flow arrangement(FA), as shown in Fig. 2a, is most frequently preferred in solvent extraction processes. In this flow arrangement, solvent recycles between extraction and stripping cascades, extracting metallic ions from aqueous feed stream and giving them off to stripping agent stream. The crosscurrent(CSC) flow arrangement possesses a great number of varieties. The specific case to be examined is shown in Fig. 2b where equal numbers of stages in the extraction and stripping cascades were used. In this flow arrangement, the number of organic recycling loops is the same as the number of stages. The feature of this flow arrangement is that the metallic ions extracted by a solvent at each stage are immediately stripped off by a stripping agent. The alternating extraction and stripping(AES) flow arrangement is shown in Fig. 2c where the extraction and stripping stages are alternately arranged in just one cascade instead of two. Therefore only one closed circulating loop for the organic stream is considered. The solvent flows through an extraction and a stripping stage in series in a closed loop, transferring metallic ions from the aqueous feed stream to the stripping agent stream. The feature of this arrangement is that the aqueous feed stream always contacts a stripped organic solvent.

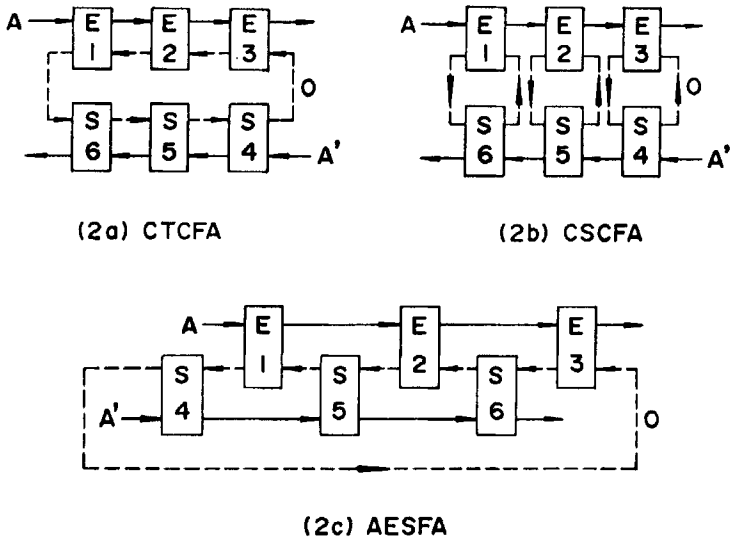

Fig. 2. Flow arrangements: (a) countercurrent; (b) crosscurrent; (c) alternating extraction and stripping

Program and Calculation

A pseudo dynamic method(7,11,12) which is based on integrating the differential equations is used in this simulation study. These equations describe unsteady-state mass balances in each stage by omitting the organic phase accumulation term. Rod(7) pointed out that at steady state the concentrations in an equilibrium stage are not dependent on the volumes of the aqueous and organic phases in the stage. The differential material balance in the extraction and stripping cascades can be expressed as follows:

For the extraction cascade,

$$\frac{dX_i}{d\bar{T}} = X_{i-1} - X_i + \frac{O}{A}(Y_k - Y_i) \qquad (2)$$

$$\begin{aligned} k &= i+1 && \text{for CTC arrangement,} \\ &= N+M+1-i && \text{for CSC arrangement} \\ &= N+1+i && \text{for AES arrangement} \end{aligned} \qquad (3)$$

where i=1,2,...N, T=(tA/V), M and N are the numbers of stages in the stripping and extraction cascades, respectively.

For the stripping cascade,

$$\frac{dX'_i}{dT} = X'_{i-1} - X'_i + \frac{O}{A'}(Y_j - Y_i) \qquad (4)$$

$$\begin{aligned} j &= i+1 && \text{for CTC arrangement, } j=1 \text{ for } i=N+M \\ &= N+M+1-i && \text{for CSC arrangement} \\ &= i-N && \text{for AES arrangement} \end{aligned} \qquad (5)$$

where i=N+1,N+2,...N+M.

The boundary conditions are as follows:

$$\begin{aligned} X_0 &= X_{in} \\ X'_{N+1} &= X'_{in} \end{aligned} \qquad (6)$$

The stage efficiencies for extraction and stripping can be expressed as follows:

$$E_{ex} = \frac{X_{i-1} - X_i}{X_{i-1} - X_i^*}, \qquad E_{st} = \frac{X'_i - X'_{i-1}}{X'^*_i - X'_{i-1}} \qquad (7)$$

RESULTS AND DISCUSSION

The differential equations given in the previous section were solved by a subroutine based on the Runge-Kutta-Gill method(13). The validity of the formulations developed above and of the computer program established in this work has been confirmed previously(9). The proposed method has been compared with the INER pilot plant data. It was found that the calculated results are in good agreement with the pilot plant data.

Comparison among the performances of those three flow arrangements will be made on the basis of the percentage recovery of uranium in the aqueous feed which is defined as:

$$R = ((X_0 - X_N)/X_0) \times 100\% \qquad (8)$$

Process Study

The relevent data of the INER process based pilot plant is listed in Table I. Fig. 3 shows the calculated effect of O/A ratio

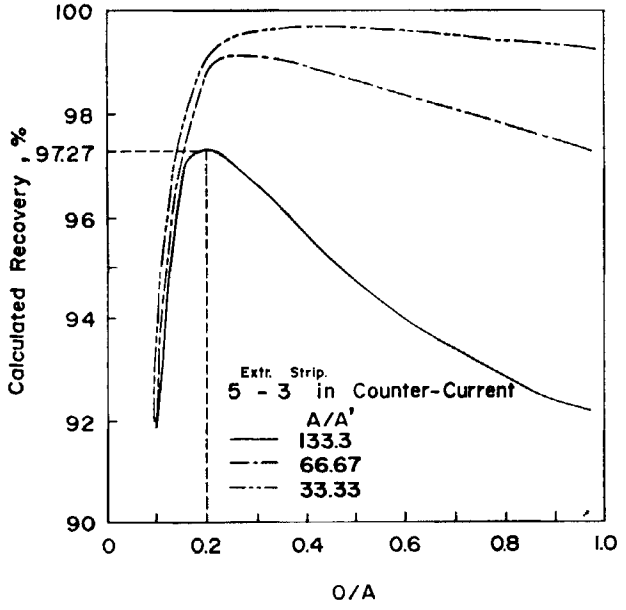

Fig. 3. Effect of O/A ratio on uranium recovery for three A/A' ratios

on uranium recovery for three A/A' ratios. This process has an optimum O/A operating condition for each A/A' value. The recovery increases steeply to a maximum level as the O/A ratio increases to 0.2, and then decreases as the O/A ratio passes 0.2. The extent of decrease in recovery as the O/A value passes beyond its optimum depends strongly on the A/A' value. The decrease of recovery is significant in the case of A/A'=133.3, but is negligible for A/A'=33.33. An optimum O/A ratio is located at 0.20 for A/A'=133.3 with a maximum recovery of 97.27%. The optimum O/A value increases as A/A' decreases. The operating condition with O/A=0.25 specified in the INER process is located near the optimum condition. But in view of a narrow optimum range of the O/A value, the expected recovery is very likely to be discounted because of a change in O/A ratio during plant operation. As an improvement to this process, it might be better to decrease the A/A' ratio to 66.7 and to increase the operating O/A ratio to 0.35. At a very low O/A value, increasing the O/A ratio will result in an increase in the interfacial area, and thus will increase the mixer efficiency(14,15). This adjustment in process conditions is expected to increase the recovery by more than 2%. In addition, a

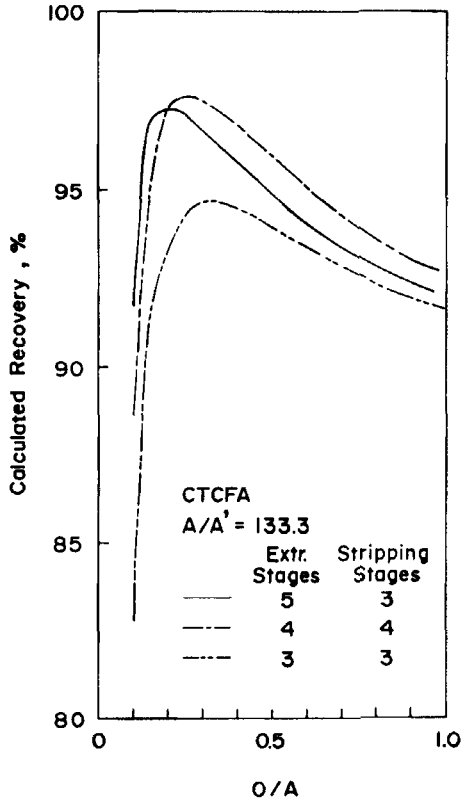

Fig. 4. Effect of CTCFA stage configuration on uranium recovery

stable operated recovery which is less sensitive to O/A changes can be obtained.

The effect of stage number and stage partition between extraction and stripping on the performance of the INER process is given in Fig. 4. The calculated results indicate that the arrangement of 4 stages in extraction cascade and 4 stages in stripping cascade is slightly better than that of 5 stages in extraction and 3 stages in stripping. The recovery with 3-3 configuration is about 2.5% lower than that with 5-3 configuration. Stripping stages need air-tight seals to keep ferrous ions from oxidizing with air. They also need insulation to keep temperature around 50°C. In view of these special considerations, 3 stripping stages is a sound choice in the INER process.

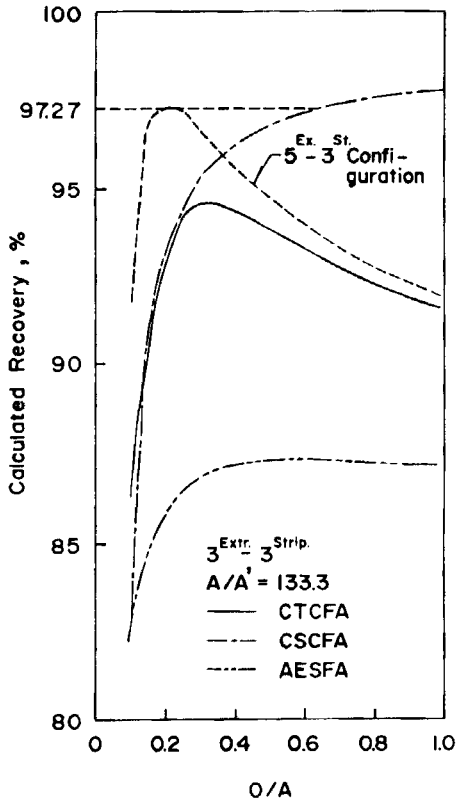

Fig. 5. Comparison of the performances as a function of O/A ratio for CTCFA, CSCFA, and AESFA

Flow Arrangement Comparison

For the CSCFA and AESFA, each possesses a great number of variations in stage configuration. This section will discuss those typical arrangements as shown in Fig. 2 only. In order to facilitate comparison, the configuration was selected that the extraction cascade has the same number of stages as the stripping cascade. Comparison of the calculated performance among the CTCFA, CSCFA, and AESFA as a function of the O/A ratio is shown in Fig. 5 for the configuration with 3 extraction stages and 3 stripping stages(3-3) at an A/A'=133.3. The performance of CTCFA with 5-3 configuration is also shown in the same figure for comparison. The calculated results clearly indicate that CSCFA is far better than

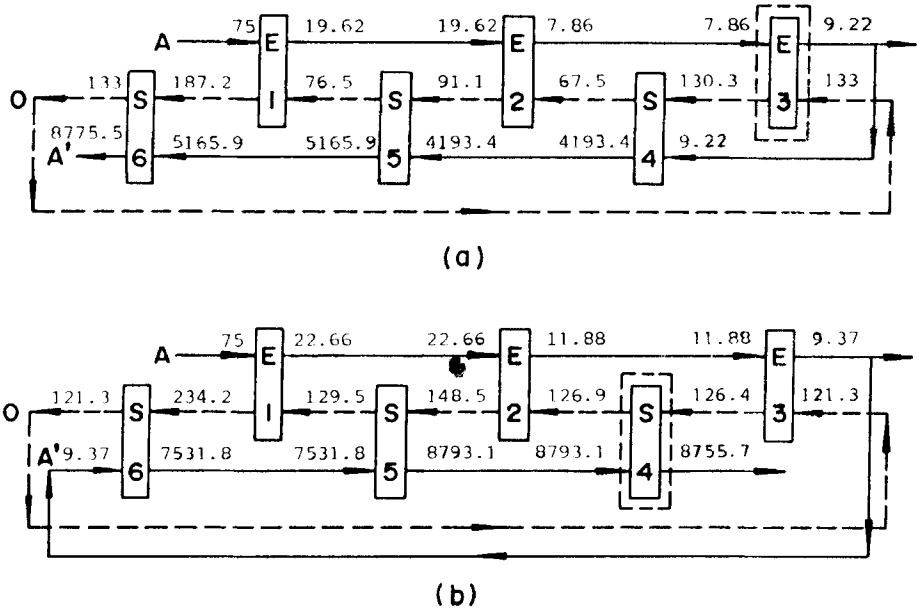

Fig. 6. The calculated concentration distributions in the AESFA at O/A=0.6
(a) A-A' countercurrent flowing
(b) A-A' cocurrent flowing

CTCFA and AESFA for O/A values larger than 0.3 from the recovery point of view. The maximum recovery of CTCFA with 5-3 configuration(97.27%) can be achieved by CSCFA with 3-3 configuration operated at O/A=0.6. Unlike CTCFA, the recovery of CSCFA always increases accompanying an increase in O/A value. It is also clear from the results of Fig. 5 that AESFA is inappropriate for the INER process under the specified operating conditions. The bad performance of the AESFA mainly results from a presaturation in either the stripping aqueous stream or the organic stream when the process is operated at high A/A' ratio. This phenomenon is shown in Fig. 6 for the concentration distribution in the extraction and stripping cascades when presaturation occurs. Fig. 6a shows the calculated concentration distribution for the case of A and A' streams flowing countercurrently, and Fig. 6b for the case of A and A' flowing cocurrently. The malfunction stages are indicated in Figs. 6a and 6b by enclosing dashed lines. Fig. 6a shows that the extraction stage E3 loses its normal function to become a stripping stage due to the presaturation of

the organic stream entering that stage. And the stripping stage S4 in Fig. 6b loses its normal function to become an extraction stage due to the presaturation of the stripping aqueous stream entering that stage. It is because this malfunction phenomenon occurs so early, at O/A=0.25(Fig. 5), that the subsequent increase in O/A does not lead to much improvement in process performance. These abnormal performances impair the efficiency of a process with the AES flow arrangement.

With the use of a compact-type multistage-mixer-settler, one organic circulating loop will need two pumps, two vessels, one heater, and one cooler for the organic phase. Thus by comparing 3-3 CSCFA with 5-3 CTCFA, it is found that CSCFA needs two more pumps, heaters, and coolers than CTCFA does. Under the same recovery, the validity of replacing 5-3 CTCFA with 3-3 CSCFA should depend on the compromise between the costs of the stage numbers decreasing and the equipment increasing such as extra pumps and heat exchangers. In addition, organic inventory is also affected by the stage number changing.

CONCLUSIONS

The INER process possesses an optimum O/A value of 0.2 with a maximum recovery of 97.27% under constant other conditions, and the operating O/A value of 0.25 is very close to this optimum O/A value. By reducing the A/A' value in the first cycle to 66.7 and raising the O/A value to 0.3 simultaneously, 2% increases in the uranium recovery are expected. In addition, a stable operating recovery, less sensitive to O/A changes, can also be obtained in accord with this adjustment. As far as the recovery is concerned, a crosscurrent flow arrangement is superior to the currently adopted countercurrent one. The recovery of the crosscurrent one always increases with increasing organic-to-aqueous flow rate ratio. A recovery of about 97.3% can also be achieved with the crosscurrent one by 3 extraction and 3 stripping stages at an O/A ratio of 0.6. The alternating extraction and stripping flow arrangement is not appropriate for use in this process because of a presaturation in either the stripping agent stream or the organic stream when the process is operated at a high A/A' ratio.

NOMENCLATURE

A	flow rate of the aqueous phase(m^3/sec)
D	distribution coefficient
E	stage efficiency defined in Eq.(7)
M	number of stages in the stripping ascade
N	number of stages in the extraction cascade
O	flow rate of the organic phase(m^3/sec)
R	percentage recovery defined in Eq.(8)
t	time(sec)
T	=(tA/V), dimensionless time

V	total volume of the mixing section of a stage(m^3)
X	concentration in the aqueous phase(kmol/m^3)
Y	concentration in the organic phase(kmol/m^3)

Indices

*	equilibrium state
ex	in extraction cascade
i,j,k,N	stage numbers
in	inlet state
M	final stage in the stripping cascade
N	final stage in the extraction cascade
st	in stripping cascade
'	in stripping cascade
0	inlet state

Abbreviations

AES	alternating extraction and stripping
CSC	crosscurrent
CTC	countercurrent
FA	flow arrangement

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