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SOLVENT EXTRACTION PROCESSES**

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# AN EXPERIMENTAL APPROACH TO THE OPTIMIZATION OF SOLVENT EXTRACTION PROCESSES

A. Ikuta\* and E.C. Costa\*

## ABSTRACT

The application of an optimization factor defined from fundamental reasoning is described in the determination of optimal choices of operating levels of process variables, and in the comparison of the performance of different experimental assemblies. The factor was defined for an extraction process as being directly proportional to the rate of transfer of the extractable species into the organic stream, inversely proportional to the rate of loss of the species in the raffinate stream, and directly proportional to the rate of production. The use of this factor permitted the extrapolation of conclusions from simple one-stage lab-scale batch experiments, to multistage pilot-scale units.

## INTRODUCTION

The maximization of rate of production and the minimization of rate of loss of valuable products in the waste streams of a production process are challenging problems which frequently defy one's skill and ingenuity. A production process operating under the conditions of maximum rate of gain or minimum rate of loss of valuable products at a fixed input rate of raw materials is said to be optimized. The search for optimized conditions, however, involves choices among alternate routes and levels of pertinent variables, which in each case must consist of optimal decisions and will ultimately determine the over-all process performance. Therefore, to establish optimal choices one must carefully select unbiased parameters which can adequately measure the process performance. As a general rule, once a suitable parameter is defined, the optimization procedure is reduced to the maximization of a function of the type<sup>1</sup>

$$P = f_1(X_i, Y_j) \quad (1)$$

where P is the response variable which measures the process performance,  $X_i$  are the controlled variables which can be varied over a range of allowable values and  $Y_j$  are uncontrollable variables peculiar to the system or apparatus being studied. In general,  $Y_j$  are constants by the very nature of the problem or can be held constant for a set of experiments, so that the resulting response function

$$P = f_2(X_i) \quad (2)$$

for different systems or apparatus can be compared. In this paper examples are given both of the maximization of P for a given system and apparatus ( $Y_j$  constant) by optimal choices of levels of controlled variables, and of the comparison of different experimental assemblies by maintaining constant the controlled variables ( $X_i$  constant) for a given constant system.

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The following work is concerned with the maximization of the functional relationship given by Equation 1 applied to solvent extraction problems, but the fundamental emphasis is placed primarily on a suitable definition of P for these processes. The work is definitely slanted toward the solvent extraction purification of nuclear materials, nevertheless the underlying theory is applicable to other extraction processes as well and can possibly be extended to many similar problems in other areas. As far as it is known to us, the approach herein described is an original contribution to the field and undoubtedly simplifies much of the laborious work of interpreting extraction data. The method not only allows optimization of qualitative decisions, but also the determination of optimal choices of operating levels of controlled variables in extraction problems. In one of the applications to be described, the method proved to be a simple and easy way of determining the optimum solvent dilution: a controversial problem which has puzzled many a worker in the past.

## THEORY

In the optimization of solvent extraction processes there are usually two well-defined problems, that of optimizing the system and external conditions (such as feed rates, feed concentrations, O/A ratio) and that of maximizing the production rate of an existing apparatus and system. In the first case the choice of adequate parameters which enable optimal decisions is a challenging problem, heretofore mostly empirically approached on the grounds of educated guesses, whereas in the second case there are several well-established measures of process performance which are in common usage. In the study of multi-stage contactors for example, HTU, HETS or stage efficiency at a fixed feed rate are the parameters most frequently encountered. These factors are an indirect measure of the rate of gain of product in the solvent stream or of the rate of loss of product in waste streams, however, whilst they are a function of the input rate, they do not indicate at what input rate the contactor is operating. They are therefore unsuitable for the pursuit of an optimization path or the maximization of P, since they are not an adequate measure of process performance. The interpretation of these data then become somewhat difficult and cumbersome, because there is the need for a parallel determination of flooding capacities and the maximized production rate does not coincide simultaneously with the conditions for minimum HETS or HTU and those for maximum throughput. By the same token, rate of production alone is an unsuitable measure of performance, because it does not take into account the rate of loss of product in waste streams.

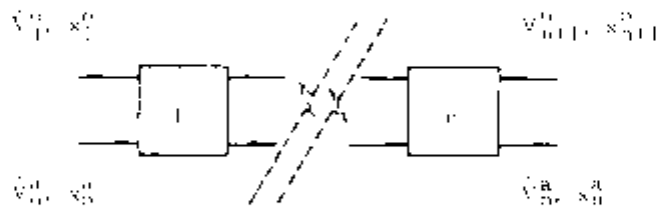
To circumvent these problems and in order to compare the performance of different contactors, there has been some attempts in the past<sup>2,3,4,5,6</sup> to employ the factor

$$(\dot{V}_{n+1}^u + \dot{V}_0^a) : \text{HETS} \quad (3)$$

in the interpretation of multi-stage contactor data. The use of this factor, however, is limited to only crude relative comparisons between contactors operating with the same extraction system, and cannot be used as a response variable in Equation 2, because HETS presents an unknown complex dependence on  $\dot{V}_{n+1}^u$  or  $\dot{V}_0^a$ . This factor has been called performance factor<sup>6</sup> and is directly proportional to the feed rate and inversely proportional to the rate of loss, since the smaller the HETS, the lower the losses and the larger the numerical value of the factor. Although arbitrarily defined and unexplainably adding two opposite flows in the numerator, the factor defined by Equation 3, contributed somewhat to the interpretation of multi-stage contactor data, although, still inadequate for the pursuit of optimum operating conditions.

In view of the aforementioned difficulties in interpreting extraction data, and adequately measuring process performance, we attempted to define in the ensuing paragraphs, based on more fundamental reasoning, another parameter which could better define the response P of an extraction process, system or apparatus.

Let us then consider, in the general case, a cascade of countercurrent continuous extractors, consisting of  $n$  discrete or continuous stages as indicated by the following diagram, in which a valuable species is being extracted from an aqueous phase fed to the first stage, to an



organic solvent fed into stage  $n$ . From our introductory remarks then, what we seek to maximize is either the rate of gain of the extractable species into the organic stream, i.e. the difference  $(\dot{V}_1^O x_1^O - \dot{V}_{n+1}^O x_{n+1}^O)$ , or the rate of transfer of the species from the aqueous to the organic phase  $(\dot{V}_n^A x_n^A - \dot{V}_{n+1}^A x_{n+1}^A)$  and to minimize the rate of loss of the extractable species in the raffinate stream  $(\dot{V}_n^A x_n^A)$ . However, the use of any of these factors alone are of no avail as a measure of  $P$ , since identical rates of gain (or rates of loss) can be obtained for different feed rates of the extractable species to the apparatus,  $x_0^A \dot{V}_0^A$ , and the performance of the apparatus is definitely dependent on the feed rate. On the other hand, a measure of process performance should be directly proportional to the rate of gain of the extractable species in the organic stream, inversely proportional to the rate of loss of product in the aqueous stream, and at the same time be a measure of the production level. We have defined a factor embracing all of these features, which we believe is an adequate measure of  $P$  for solvent extraction processes, and to which we have assigned the name optimization factor ( $F_{opt}$ ). One can then write

$$\text{(optimization factor)} \propto \left( \frac{\text{rate of gain}}{\text{rate of loss}} \right) \times \text{(rate of production)} \quad (4)$$

which for a cascade of continuous extractors becomes

$$F = K \left[ (\dot{V}_1^O x_1^O - x_{n+1}^O \dot{V}_{n+1}^O) / (x_n^A \dot{V}_n^A) \right] (\dot{V}_1^O x_1^O) \quad (5)$$

or

$$F_{opt} = \left[ (\dot{V}_1^O x_1^O - x_{n+1}^O \dot{V}_{n+1}^O) / (x_n^A \dot{V}_n^A) \right] (\dot{V}_1^O x_1^O) \quad (6)$$

As a measure of process performance,  $F_{opt}$  is a function of all variables affecting the behavior of the apparatus and system, as defined by Equation 2, and the maximization of  $F_{opt}$  can be done by the usual procedures. However, once  $F_{opt}$  is maximized, the question still remains whether  $F_{opt}$  is an adequate and unbiased measure of process performance. This can be verified by parametric deviations along the axis of the controlled variable being optimized, around the value which maximizes  $F_{opt}$ , and observing the value of the difference between the rate of gain

in the solvent stream and the rate of loss in the aqueous stream ( $\dot{V}_j^o x_1^o - \dot{V}_n^a x_n^a$ ). If this difference is maximized for the same value of the controlled variable which maximizes  $F_{opt}$ , then  $F_{opt}$  should really be an unbiased measure of the process under study.

To further visualize the problem of maximizing  $F_{opt}$ , let us consider an extraction problem, say the extraction of uranyl nitrate, thorium nitrate or zirconyl nitrate from an aqueous nitric acid solution into a n-tributylphosphate-inert diluent organic phase. We have then fixed our extraction system. Now, say we are performing the extraction in an existing battery of mixer-settler contactors, so that the  $Y_j$ 's are constants. Thus  $F_{opt}$  becomes

$$F_{opt} = f_3(X_1) \quad (7)$$

where  $X_1$  are the controlled variables affecting  $F_{opt}$ , such as the organic feed flowrate ( $\dot{V}_{n+1}^o$ ), the aqueous feed flowrate ( $\dot{V}_0^a$ ) or the ratio of organic to aqueous feed flowrates ( $\dot{V}_{n+1}^o/\dot{V}_0^a$ ), plus all other factors affecting the extraction factor,  $E_{\mu}^o$ , of the extractable species. In this problem  $F_{opt}$  would generally be an equation of the form

$$F_{opt} = f_3(\dot{V}_{n+1}^o, \dot{V}_0^a, \dot{V}_{n+1}^o/\dot{V}_0^a, x_0^a, x_{\text{salt}}^a, x_{\text{aq}}^a, x_{\text{TBP}}^o, T) \quad (8)$$

The function defined by Equation 8 can then be maximized by any of the usual procedures for maximizing a response function in several independent variables, in order to find an absolute maximum in  $F_{opt}$ . In general, however, one must place constraints on the levels of some of the controlled variables, for example on the maximum working temperature to prevent fire hazards or degradation of solvents, or on ( $\dot{V}_{n+1}^o/\dot{V}_0^a$ ),  $x_0^a$  or  $x_{\text{TBP}}^o$  which might cause the segregation of a diluent-rich phase, or on  $\dot{V}_{n+1}^o$  which can cause flooding of the apparatus. Therefore, most of the time, in the optimization of solvent extraction processes, one is concerned with local maxima in  $F_{opt}$ , since constraints are placed on some of the variables. The existence of maxima in  $F_{opt}$  along the axes of the controlled variables is warranted by Rolle's theorem, when there are no discontinuities on the response surface in the region of experimentation, as can be easily verified by an analysis of the change of  $F_{opt}$  for each of the variables listed in Equation 8. The application of  $F_{opt}$  is illustrated in the following section.

## EXPERIMENTAL WORK AND ANALYSIS OF THE DATA

The optimization factor as defined by Equation 6 has been applied in the determination of optimal choices for two different extraction systems: 1) the extraction of thorium nitrate from an aqueous 1 N  $\text{HNO}_3$  solution and 2) the extraction of  $\text{HNO}_3$  from an approximately 3 N aqueous solution. In both cases a fresh organic phase (i.e.  $x_{n+1}^o = 0$ ), consisting of a mixture of n-tributylphosphate (TBP) with Varsol was employed as the extracting phase. In the extraction of thorium nitrate, the apparatus and system were kept constants ( $Y_j$  constant), and the problems consisted of choosing and comparing the optimal organic solvent dilution in three different apparatus: a one-stage batch contactor, a one-stage continuous countercurrent contactor and a four-stage continuous countercurrent contactor, and of choosing the optimal thorium nitrate concentration in a 1 N  $\text{HNO}_3$  aqueous solution from the data of a one-stage batch contactor. In the extraction of  $\text{HNO}_3$  from an aqueous solution, the data from the work of Brill and Costa<sup>6</sup> was recalculated by means of the optimization factor. Their work was concerned with the establishment of an optimal choice among different cartridges for a given perforated-plate pulsed extraction column and the determination of the optimum amplitude-frequency product ( $af$ ) for each cartridge at a fixed input rate to the column. In our

work we shall employ only part of their data and our results will be compared with their findings

### 1) Extraction of Thorium Nitrate

**Choice of the Organic Solvent Dilution.** This part of the work has a double purpose, that of illustrating the establishment of a local maximum for one of the variables when other controlled variables are constrained, and that of comparing the conclusions drawn from the use of different experimental setups, in order to assess the validity of the conclusions arrived at by employing a simple one stage batch contactor.

The batch contactor consisted of a 3.5 cm I.D. glass cylinder provide with a ground-glass stopcock in the bottom for draining the liquids at the end of a run, and an external heating jacket through which water, from a constant temperature bath, was circulated. The temperature in all experiments was maintained at the 35°C level. Constant agitation was provided by a turbine impeller connected to a motor and a variable voltage transformer. The same speed of agitation was used in all experiments. In each case, 60 ml of the fresh organic phase was contacted with 30 ml of an aqueous phase (O/A=2) of thorium nitrate containing 300 g/l ThO<sub>2</sub> and 1 N HNO<sub>3</sub>. The experiments consisted of mixing the two phases for successive periods of 3 minutes each and observing the decantation time until constant readings were obtained. Generally, after two mixing periods the decantation time remained constant within the experimental error. Samples of the organic and aqueous phases were then collected and analysed. The criterion for determining the end of the settling period was the ceasing of vertical motion of the interface between the phases. Decantation times could be reproduced, in the majority of the runs, within ± 0.02 min. The data for these experiments are reported in Table 1, along with the calculated values for the optimization factor, and shown graphically in Figure 1. The observed maximum in F<sub>opt</sub> corresponded approximately to a 50 v% TBP-in-Varsol organic phase. The optimization factor employed in these calculations was defined as follows

$$F_{opt} = (x^a V^a / x^b V^b) x^c (V^d / t_{dec}) \quad (9)$$

and had the units of g ThO<sub>2</sub>/min

TABLE 1

Choice of the Organic Phase Concentration Batch Contactor Data. Aqueous Phase: 300g/l ThO<sub>2</sub>, 1 N HNO<sub>3</sub> O/A=2. Organic Phase Volume: 60 ml Temperature: 35°C

<sup>o</sup> <sub>TBP</sub> lv%	<sup>o</sup> <sub>Th(NO<sub>3</sub>)<sub>4</sub></sub> (g/l ThO <sub>2</sub> )	<sup>a</sup> <sub>Th(NO<sub>3</sub>)<sub>4</sub></sub> (g/l ThO <sub>2</sub> )	t <sub>dec</sub> (min)	F <sub>opt</sub> (g/min ThO <sub>2</sub> )
20	45.0	217.6	0.45	2.5
40	83.7	133.9	0.75	8.4
50	95.0	107.9	0.97	10.4
60	111.0	77.8	2.18	8.7
80	124.2	49.8	>240	< 0.15



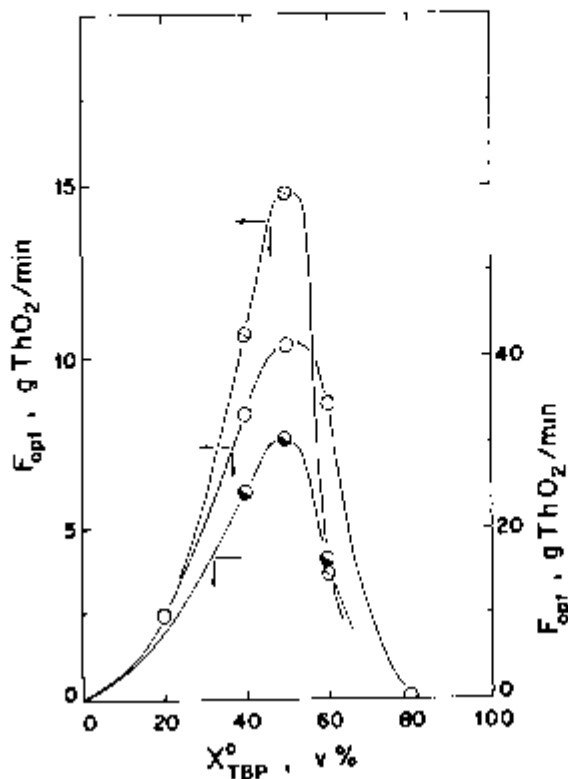


FIGURE 1

Choice of the Organic Phase Concentration for a 300g/l ThO<sub>2</sub>, 1 N HNO<sub>3</sub> Aqueous Phase.

- Batch contactor
- ◐ Continuous one-stage contactor
- Continuous multi-stage contactor

The one-stage continuous contactor consisted of a mixing chamber and a separate settling chamber. The mixing chamber was the same employed in the batch experiments, with an overflow outlet which led to the settling chamber. The volume of this chamber was such as to provide a mean mixing time of about 5 minutes at the highest flows. Both the mixing and settling chambers were provided with external water-heating jackets. The mixture leaving the mixing chamber flowed by gravity into the settling chamber where the height of the interface was controlled by manual displacement of the vertical position of the aqueous phase overflow. The experiments consisted of varying the input flow rates in the ratio  $O/A=2$  and maintaining the position of the interface constant, so as to provide a 60 ml settling volume for the organic phase. Plotting the input flow rates against the entrainment of the aqueous phase in the organic phase, permitted the determination of the ratios corresponding to 1 v% entrainment. Experiments were performed then at these rates and samples of both phases at equilibrium conditions were collected and analyzed. The data for these experiments are reported in Table 2 and shown graphically in Figure 1. The maximum in  $F_{opt}$  also occurred at an approximate

value of 50 v% TBP-in-Varsol. The optimization factor had the units of g ThO<sub>2</sub>/min and was defined in this case as

$$F_{opt} = (x^D v^D / x^A v^A) x^O \dot{V}^O \quad (10)$$

TABLE 2

Choice of the Organic Phase Concentration. Continuous One-stage Contactor  
Data at 1% Entrainment of the Aqueous Phase. Aqueous Phase: 300g/l ThO<sub>2</sub>,  
1 N HNO<sub>3</sub>. O/A=2. Organic Phase Decantation Volume: 60 ml. Temperature:  
35°C.

$x_{TBP}^O$ [v%]	$x_{Th(NO_3)_4}^O$ [g/l ThO <sub>2</sub> ]	$x_{Th(NO_3)_4}^D$ [g/l ThO <sub>2</sub> ]	$V_D$ [ml/min]	$F_{opt}$ [g/min ThO <sub>2</sub> ]
40	84.6	131.6	98.6	10.7
50	91.0	117.9	75.0	14.8
60	113.0	87.4	22.6	3.7

The four-stage continuous countercurrent contactor consisted of a section sealed off from a Model BR-001 16-stage Lucite mixer-settler contactor, manufactured by Ets. Deschamps-Chalande, St. Quen, France. The aqueous and organic phases were steadily fed at a constant temperature of 35°C in the ratio O/A=2. The flows were varied in order to cause different entrainments of the aqueous phase in the organic phase. The level of the interface between phases was kept constant in all stages, so as to provide the same decantation volume. After the battery reached equilibrium, samples were collected and analyzed, and the entrainment measured. A 5 v% entrainment level was used for the analysis of the data. The data are reported in Table 3 and in Figure 1. In this case, the maximum in  $F_{opt}$  also occurred at an

TABLE 3

Choice of the Organic Phase Concentration. Continuous Multi-stage Contactor  
Data at 5 v% Entrainment of the Aqueous Phase. Aqueous Phase:  
300g/l ThO<sub>2</sub>, 1 N HNO<sub>3</sub>. O/A=2. Temperature: 35°C.

$x_{TBP}^D$ [v%]	$x_{Th(NO_3)_4}^O$ [g/l ThO <sub>2</sub> ]	$x_{Th(NO_3)_4}^A$ [g/l ThO <sub>2</sub> ]	$V_{n+1}^O$ [ml/min]	$F_{opt}$ [g/min ThO <sub>2</sub> ]
40	129.3	30.2	22.5	24.5
50	132.6	22.4	19.5	30.6
60	135.5	10.6	4.8	16.6

approximately 50 v% TBP-in-Varsol concentration. The optimization factor used for the calculations was defined as

$$F_{opt} = (x_1^0 v_1^0 / x_4^d v_4^d) \cdot x_1^0 v_1^0 \quad (11)$$

The results reported in Figure 1 were amazingly coincident. There were differences as expected on the magnitude of the optimization factors, since different apparatuses were used, however, the agreement as to the best solvent dilution was remarkable. One can therefore conclude that simple batch experiments can supply the necessary information for optimal choices of the levels of the controlled variables, and the data when correctly interpreted can be extrapolated to multi-stage extraction units.

In order to further evaluate the conclusions drawn from the application of the optimization factor and to verify whether it is an unbiased measure of the performance of the extraction process, several other measures of process performance were calculated from the data in Table 1. These new data are reported in Table 4. Column 2 in this table is a measure of the rate of gain of the thorium nitrate into the organic phase per cycle, while the third column is a measure of the rate of loss per cycle. An analysis of the first column alone, would indicate that the lower TBP concentrations would favor the production rate, whereas column 3 indicates

TABLE 4

Comparison between different factors used in the interpretation of extraction data from a batch contactor.

$x_{TBP}^0$ (v%)	$x_{Th(NO_3)_4}^0 v_1^0 / t_{dec}$ (g/min ThO <sub>2</sub> )	$x_{Th(NO_3)_4}^d v_4^d / t_{dec}$ (g/min ThO <sub>2</sub> )	$(x_1^0 v_1^0 \cdot x_4^d v_4^d) / t_{dec}$ (g/min ThO <sub>2</sub> )	$E_{th}^0$	$E_{th}^0 / t_{dec}$ (min <sup>-1</sup> )	$F_{opt}$ (g/min ThO <sub>2</sub> )
20	6.0	14.5	-8.5	0.41	0.91	2.5
40	6.7	5.4	1.3	1.25	1.67	8.4
50	5.9	3.33	2.6	1.76	1.81	10.4
60	3.05	1.07	2.0	2.85	1.31	8.7
80	0.03	<0.01	>0.02	4.99	<0.02	<0.15

that the rates of loss increase with decreasing TBP concentrations. In fact, at the lower TBP concentrations we lose more thorium nitrate than we extract. Hence, if lower TBP concentrations favor the rate of production and higher TBP concentrations decrease the rate of loss, there must be an intermediate concentration which is a compromise between these rates and maximizes the rate of gain. This is indeed the case, as proved by the difference between the rate of production and the rate of loss in column 4, the ratio between gain and loss per unit time reported in column 6, as well as the optimization factor reported in column 7. All maxima in columns 4, 6 and 7 occurred at approximately 50 v%. Similar calculations for the data in Tables 2 and 3 yield identical results. One can therefore conclude that the optimization factor herein defined is a true measure of the performance of the extraction process.

**Choice of the Aqueous Phase Concentrations.** The simple one-stage batch contactor used in the previous experiments were employed now for the maximization of  $F_{opt}$  by varying the thorium nitrate content of a 1 N  $HNO_3$  aqueous solution. The organic phase was a fresh 50 v% TBP-in-Varsol solution. The O/A was maintained at 2/1 and the temperature kept at the 35°C level. The experimental data are reported in Table 5 and in Figure 2. The maximum in  $F_{opt}$  occurred at approximately 290 g/l  $ThO_2$  for the solution studied. The optimization factor used in the calculations was the same as defined by Equation 9. This factor proved once more to be a simple and effective way of interpreting the experimental extraction data.

TABLE 5

Choice of the  $Th(NO_3)_4$  Concentration in the Aqueous Phase. Batch Contactor Data. Organic Phase: 50 v% TBP-in-Varsol, O/A=2. Organic Phase Volume: 60 ml. Temperature: 35°C.

$x_{initial}^a$ (1N $HNO_3$ ) [g/l $ThO_2$ ]	$t_{dec}$ (min)	$x^b$ [g/l $ThO_2$ ]	$x^d$ [g/l $ThO_2$ ]	$F_{opt}$ (g/min $ThO_2$ )
400	2.73	122.2	152.7	4.3
300	1.10	95.0	108.0	9.4
180	1.12	62.2	52.9	7.8
90	0.96	30.8	28.9	4.7
45	0.73	14.3	16.8	2.0
18	0.70	5.1	7.3	0.61

## 2) Extraction of Nitric Acid

**Choice of the Optimum  $af$  for Different Cartridges.** The data for three different pulsed column cartridges used in the extraction of  $HNO_3$  from an aqueous solution was taken from the work of Brill and Costa<sup>6</sup>. The original experimental data from this work for an all-stainless steel cartridge, an all-Lucite cartridge and a mixed cartridge consisting of alternate pairs of stainless steel and Lucite plates are given in Tables 6, 7 and 8, along with the original values of HETS, and shown graphically in Figure 3. The HETS data was determined at a constant total throughput of 22 l/hr [0.88 l hr<sup>-1</sup>cm<sup>-2</sup>] in all experiments, therefore the choice of the best  $af$  is valid only for these conditions. From the plot of HETS vs  $af$  in Figure 3, Brill and Costa determined the optimum  $af$ 's for the prevailing operating conditions, as the ones which yielded a minimum value of HETS. These values can easily be found from Figure 3. Of course, the calculation of HETS's involved the determination of an equilibrium diagram for the system, an operating and the usual McCabe-Thiele determination of the number of theoretical stages.

We have recalculated the data in Tables 6, 7 and 8 by means of the optimization factor, employing the general definition given by Equation 6. The results are given in column 10 of these tables and shown graphically in Figure 4, along with the HETS data. Comparison between the curves of HETS and  $F_{opt}$  versus  $af$  for each cartridge, immediately shows that the  $af$  value which yields the minimum HETS is identical with the one that maximizes  $F_{opt}$ . This is a

**TABLE 6**

Data for the Stainless Steel Cartridge,  $44.9 \pm 0.1$  v% TBP in Varso, O/A = 10 Pulse frequency, 102.8 cy/min, Temperature: 25°C.

$f$ /sec	$x_{n+1}^v$ {N}	$x_1^d$ {N}	$x_0^a$ {N}	$x_n^a$ {N}	$V_1^o$ {l/hr}	$V_n^i$ {l/hr}	$V_{n+1}^o$ or Flooding {l/hr}	HETS at $V_1^o$ {cm}	$F_{opt}$ {eq-g/hr}	$\Gamma_{opt}$ {eq-g/hr}
5	0.001	0.308	3.01	0.117	19.6	1.95		28	180	
3	0.001	0.296	2.98	0.099	19.9	1.95	-90	26	180	813
2	0.001	0.308	2.98	0.104	20.2	1.97	37	25	189	346
10	0.001	0.284	2.98	0.099	20.0	1.95	28	26	167	119

**TABLE 7**

Data for the Lucite Cartridge, 45.1 ± 0.1 v% TBP-in-Varsol, O/A=10, Pulse Frequency: 102.8 cy/min, Temperature: 25°C

$v$ (sec)	$x_{n+1}^o$ (N)	$x_1^o$ (N)	$x_o^a$ (N)	$x_n^a$ (N)	$V_1^o$ (l/hr)	$V_n^a$ (l/hr)	$V_{n+1}^o$ at flooding (l/hr)	HETS at $V_1^o$ (cm)	$F_{opt}$ (cc-g/hr)	$F_{opt}$ (cc-g/hr)
56	0.001	0.301	3.00	0.167	19.8	1.88	-	38	113	-
25	0.001	0.305	3.00	0.120	19.9	2.03	48	30	151	364
93	0.002	0.304	3.00	0.126	20.3	1.99	34	31	152	254
62	0.002	0.300	3.00	0.190	19.7	1.91	24	40	96	117

**TABLE 8**

Data for the Mixed Cartridge.  $45.0 \pm 0.1$  v/v% TBP-in-Varsol.  $D/A=10$ . Pulse frequency: 102.8 cy/min.  
Temperature: 25°C

$t$ (sec)	$x_{n+1}^0$ (N)	$x_1^0$ (N)	$x_0^a$ (N)	$x_n^a$ (N)	$\dot{V}_1^a$ (l/hr)	$\dot{V}_n^a$ (l/hr)	$\dot{V}_{n+1}^a$ at flooding (l/hr)	HFTS at $\dot{V}_1^a$ (cm)	$F_{opt}$ (eq-g/hr)	$F_{opt}$ (eq-g/hr)
25	0.000	0.302	2.94	0.126	20.0	2.00	75	31	144	542
93	0.004	0.287	2.96	0.101	20.0	2.00	47	25	167	375
52	0.005	0.312	2.96	0.123	20.4	2.04	28	25	161	221
30	0.005	0.297	2.96	0.135	20.2	1.90	21	28	141	135

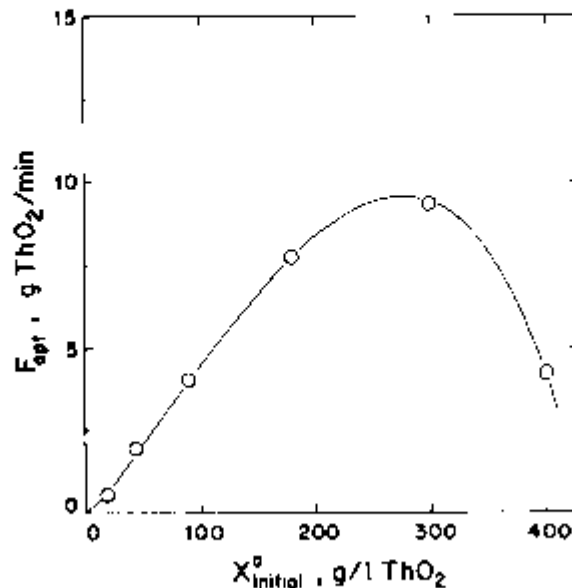


FIGURE 2

Choice of the Aqueous Phase Concentration for a 50 v%  
TBP-in-Varsol Organic Phase

remarkable result in view of the ease of interpretation of the experimental data by means of the optimization factor. We have therefore, now under pilot-scale conditions in a multi-stage countercurrent continuous contactor, found definitive evidence that  $F_{\text{opt}}$  is a true, unbiased measure of the performance of the extraction process.

**Optimal Choice Among Cartridges.** When one operates a pulsed-column contactor under a fixed total throughput, the choice of the best cartridge can be done by comparing the maxima in  $F_{\text{opt}}$ . Different cartridges, apparatuses or systems can only be compared under optimized conditions. Therefore, one can easily see from Figure 4 that the stainless steel cartridge yields the highest value of  $F_{\text{opt}}$  at the corresponding maximum. The stainless steel cartridge is therefore an optimal choice among the three cartridges studied. Costa and Brill arrived at the same conclusion interpreting the data by means of the factor defined by Equation 3. Since this factor involves the total throughput at flooding and the HETS determined at a fixed flowrate far from flooding, the results are subject to a certain amount of uncertainty, nevertheless their conclusions were identical to the ones reported in this paper. To further verify the behavior of  $F_{\text{opt}}$  we have calculated another optimization factor based on flooding rates, as follows:

$$F_{\text{flood}} = (x_1^0 V_1^0 / x_n^0 V_n^0) (x_1^0 / V_{n+1}^0) \quad \text{at flooding} \quad (12)$$

The implicit assumption here, like in the use of Equation 3, is that the efficiency of the pulsed column is little affected by the flowrate. The calculated data are reported in the last column of



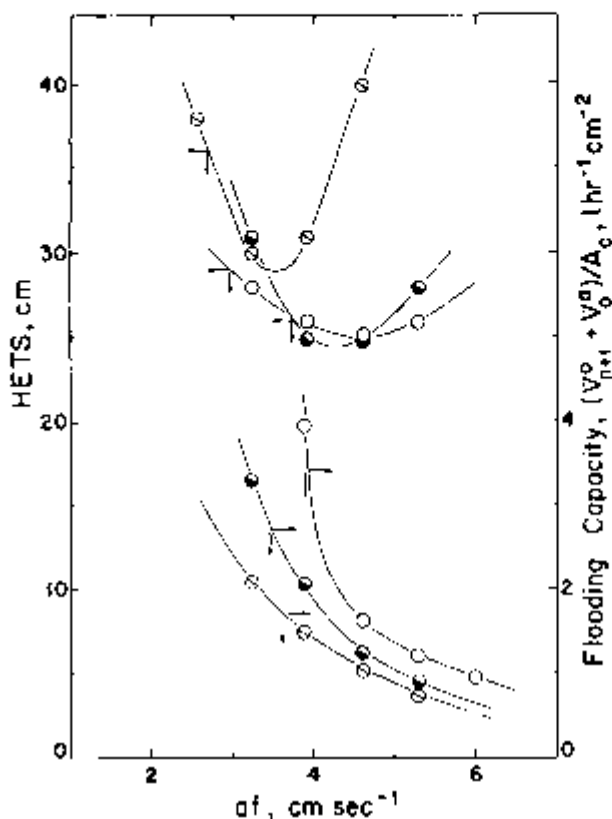


FIGURE 3

HETS and Flooding Capacity Data for Different Cartridges.

- Stainless steel cartridge
- ◐ Lignite cartridge
- Mixed cartridge

Tables 6, 7 and 8, and plotted in Figure 5. A glance at Figure 5 immediately indicates that the stainless steel cartridge is by far the best choice for the system studied.

### CONCLUSIONS

There are a number of conclusions to be drawn from the definition of the optimization factor and the applications described in this work.

In defining the optimization factor, we attempted to approach the problem of characterizing process performance from the fundamental reasoning that whatever variable affects the performance of a process, its effect, when the variable is subject to a change in level (qualitative or quantitative), must ultimately affect the ratio of the rate of gain to rate of loss of product at a certain operation level. This is very fortunate, since the optimization factor can now be applied in the choice of the system of extraction, in the choice of an extraction contactor or in the comparison of contactors, as well as in the determination of optimal levels

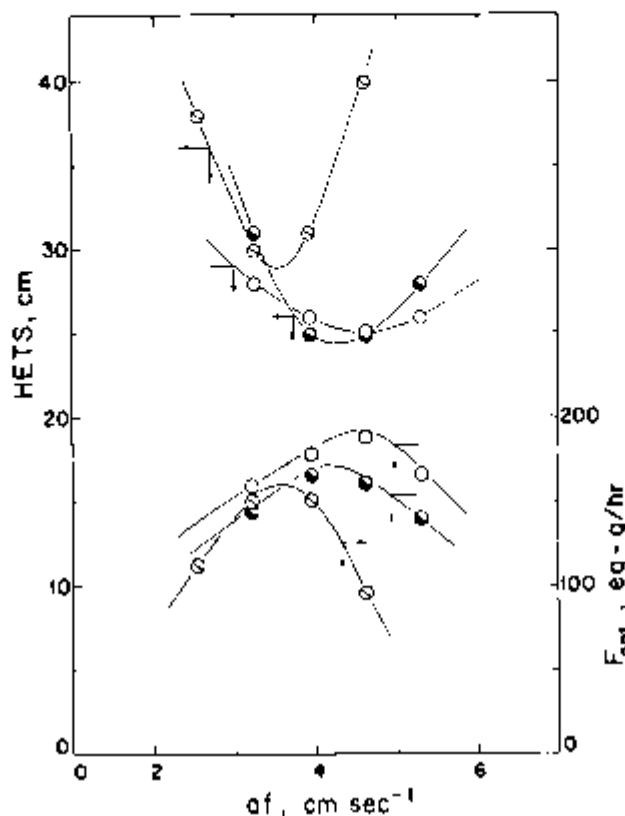


FIGURE 4

Choice of optimum  $af$  based on HETS and  $F_{opt}$  data.

- Stainless steel cartridge
- ◐ Lucite cartridge
- Mixed cartridge

for operating variables. Many of the examples given in the text illustrate these assertions. Furthermore, if the applicability of the optimization factor can be extended and generalized to all extraction systems, as we hope to investigate in future works, we have then found a truly unified way of optimizing all steps of an extraction process.

Two applications of the optimization factor mentioned in the text which deserve special attention are the choice of the optimum solvent dilution, as illustrated in the extraction of thorium nitrate by a mixture of TBP-Varsol, and the choice of the best cartridge from a set in the operation of a pulsed extraction column. In the former case, the optimum dilution was determined and confirmed by experiments in three widely different contactors, therefore solving this age-long problem which has defied many investigators, whereas in the latter case the optimization factor proved to be a simple and effective way of interpreting extraction data, instead of the laborious use of the HETS method.

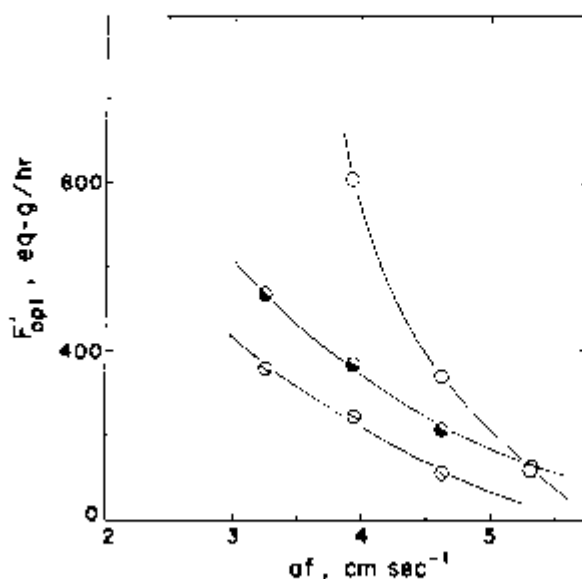


FIGURE 5

Optimization factors at flooding

- Stainless steel cartridge
- ◐ Lucite cartridge
- ◑ Mixed cartridge

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## NOMENCLATURE

- a total amplitude of motion in a pulsed column extractor, cm
- af amplitude-frequency product, cm sec<sup>-1</sup>
- E<sup>0</sup> extraction factor from the aqueous to the organic phase
- f<sup>a</sup> frequency of pulse in a pulsed extractor, cycles/sec
- f<sub>1</sub>, f<sub>2</sub>, f<sub>3</sub> functional relationships relating the variables X<sub>j</sub> and Y<sub>j</sub> to P
- F K times F<sub>opt</sub>
- F<sub>opt</sub> optimization factor, mass/time
- F<sub>opt</sub> optimization factor defined by Eq. 12, eq-g/hr
- HETS height equivalent of a theoretical stage, cm
- HTU height of a mass-transfer unit, length

K	proportionality constant
O/A	ratio of the organic to aqueous phase volumes or volumetric flowrates
P	a measure of process performance
t	time, minute
T	temperature, °C
v%	fractional volume percentage of TBP in a mixture TBP-inert diluent, %
V	volume, ml
V	volumetric flowrate, ml/min
X <sub>i</sub>	controlled variables in an extraction process
Y <sub>i</sub>	uncontrolled variables in an extraction process

#### subscripts:

0, 1, ..., n, n+1	refer to stages in a multistage contactor
dec	refer to the decantation time or decantation volume
salt.ag.	refer to salting agents

#### superscripts:

a	refer to the aqueous phase
o	refer to the organic phase

## RESUMO

A aplicação de um fator de otimização, definido a partir de considerações fundamentais, é descrita na determinação de níveis otimizados de variáveis de processo e na comparação do desempenho de diferentes aparelhos de extração. O fator definido para um processo de extração é diretamente proporcional à velocidade de transferência da espécie extraível para a fase orgânica, inversamente proporcional à velocidade de perda da espécie no refinado, e diretamente proporcional à velocidade de produção.

O uso deste fator permitiu a extrapolação de conclusões obtidas em contactadores de laboratório de uma etapa, para unidades piloto multi-etapas.

## RÉSUMÉ

L'application d'un facteur d'optimisation, défini à partir de considérations fondamentales, est décrite dans la détermination de niveaux optimisés des variables du processus et dans la comparaison du comportement de différents appareils d'extraction.

Le facteur défini pour un processus d'extraction est directement proportionnel à la vitesse de transfert de l'espèce qu'il est possible d'extraire de la phase organique, inversement proportionnel à la vitesse de perte de l'espèce dans le matériau raffiné et directement proportionnel à la vitesse de production. L'emploi de ce facteur a permis l'extrapolation de conclusions obtenues avec des contacteurs de laboratoire à une étape, à des unités pilotes à plusieurs étapes.

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