AN OPTIMIZATION STUDY OF THE PRECIPITATION OF THORIUM OXALATE

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ABSTRACT

The maximization of the effects of 4 variables (time, temperature, initial free HNO_3 concentration and excess oxalic acid) on the filtration rate of $Th(C_2O_4)_2.6H_2O$ precipitated from a 60g ThO_2/l thorium nitrate solution has been studied. The precipitations were carried out in a batch agitated lab-scale reactor at constant weight of $Th(C_2O_4)_2.6H_2O$, while in the filtration step a constant volume was filtered under constant vacuum through filter papers of the same lot.

The optimization was effected by the Steepest Ascent Method employing data from a half-replicate of a 2^4 factorial design. A total of 25 tests were required. The analysis of the data indicated that maximum filtration rate for a 60g ThO_2/l solution is obtained by precipitation at $60 \pm 4\,^{o}C$ in a $3.1 \pm 0.3N$ HNO_3 solution, using $20 \pm 3\%$ excess oxalic acid with a precipitation-digestion period of 28 ± 2 min. A check on these data was obtained by individual parametric variation around the maximum. Solutions containing 40 and 80 g ThO_2/l were also precipitated at these conditions, however, results indicated the need for optimization at each particular solute concentration level.

1. INTRODUCTION

The precipitation of thorium oxalate from aqueous acidic solutions of thorium nitrate is a common intermediate step occurring in the production of nuclear grade thorium dioxide. The requirements of high-purity and low production costs makes it necessary to establish suitable precipitation conditions for obtaining an easily filterable precipitate, which can be readily washed free of its accompanying soluble impurities.

Frequently in the precipitation of thorium oxalate, under inadequate conditions, a thixotropic paste or a thick slurry, or even a fine suspension of this salt is obtained which is difficult to handle and can cause much trouble in the subsequent filtration and washing operations. Precipitation of thorium oxalate by the

addition of oxalic acid to a thorium nitrate solution can occur under a variety of conditions, but the structure and physical characterists of the resulting oxalate are strongly affected by precipitation conditions. The salt formed at the conditions commonly encountered is the hexahydrate, $Th(C_2O_4)_2.6H_2O$, with a crystalline structure varying from an amorphous powder to quadratic prisms, or frequently mixtures of both forms with varying crystal sizes, depending on precipitation conditions.

A brief historical review of the preparation of this salt can be found in reference[1]. Its preparation was initially described by Berzélius, dating back to 1829. More recently, in connection with the production of fertile materials, the preparation of nuclear grade thorium oxalate was described by Lipkind and Newton[2], Ayers[3], Tucker and Wilhelm[4], Haas et al.[5] and Kinoshita et al.[6].

According to the work of Lipkind and Newton[2], crystalline thorium oxalate with good filtration characteristics can be obtained by adjusting the initial free HNO_3 concentration to suitable levels, depending on the Th^{+4} concentration and the precipitation temperature, when using a 5% excess of oxalic acid. For example, a 43g Th^{+4}/1 solution could be satisfactorily precipitated at 25° or 75°C by using a 6N HNO_3 solution and a 5% excess oxalic acid. Filtrations, in this case, were conducted under vacuum on a Büchner funnel.

Ayers[3] studied the excess oxalic acid requirements for quantitatively precipitating the oxalate from boiling solutions containing from 0.1 to 2.4N HNO_3, and from 5 to 7.5 g Th^{+4}/1. According to his findings, if the solution is 0.2N HNO_3, 100% excess oxalic acid is adequate, whereas a 1.8N HNO_3 solution would require a 400% excess.

Tucker and Wilhelm[4], in the course of the development of the technology of a thorium purification process, obtained crystalline precipitates from solutions with thorium concentrations from

0.9 to 1.65 lb/gal, by using a 4/1 ratio of moles of HNO_3 to moles of thorium and a 10% excess oxalic acid, after stirring the slurry for 1 1/2hr. Solutions above or below that range of concentrations yielded thixotropic precipitates, which were difficult to filter and troublesome to handle.

More recently, Haas et al.[5] described the precipitation of a thorium oxalate of controlled particle size, in connection with the development work on the production of suitable ThO_2 for use in homogeneous reactor blankets. Their results indicate that satisfactory precipitates are obtained by precipitation of a 1M $Th(NO_3)_4$ solution with a 1M oxalic acid solution at 10-15°C, with a precipitation time of 3 hours and a digestion time of 6 hours at 75°C.

Kinoshita et al.[6] studied the effect of the precipitation temperature on the particle size distribution of the resulting thorium oxalate. Precipitations at 6, 23 and 50°C from a 1M solution of thorium nitrate with a 1M solution of oxalic acid, indicated that at 6 and 23°C particle distribution maxima occurred at 0.8 μ, while at 50°C the maximum occurred in the vicinity of 2μ. At 100°C the average particle size was much larger and ranged from 5-10μ.

From the comparison between the precipitation conditions proposed by the different investigators described above, one can see that there is no general agreement as to the best conditions, but that there is a certain latitude in the choice of the levels of the variables to give more or less satisfactory results.

In the present work we have endeavoured to establish the best precipitation conditions for a certain concentration level of thorium nitrate in the aqueous solution, in order to obtain a maximized filtration rate. The problem was approached by the Steepest Ascent Method developed by Box and Wilson[7] employing data from a fractional factorial design at two levels of the variables.

The variables chosen for this study were the precipitation-digestion time, the temperature, the initial free HNO_3 concentration and the excess oxalic acid.

2. EXPERIMENTAL

The precipitations were carried out in a lab-scale batch agitated reactor, keeping constant the initial concentration of the thorium nitrate solution (60g ThO_2/l), the concentration of the oxalic acid feed solution (100g/l), the rate of addition of the oxalic acid solution (70 ml/min), the speed of agitation, the amount of thorium oxalate hexahydrate formed upon precipitation (58g) and the over-all solution volume (1250 ml), in the absence of initial crystals ("seeds") of thorium oxalate. The reactor consisted of a 3 liter beaker provided with an agitator and thermometer, all immersed in a constant temperature water-bath. The precipitation temperature could be controlled to within $\pm$ 1°C of the desired level with this arrangement.

Filtration was carried out at the precipitation temperature in an 11 cm diameter Büchner funnel, at approximately constant manometric depression (51 mm Hg). At the end of a run the reactor contents were dumped all at once on top of the funnel and suction immediately started. Time was recorded from this moment on. Schleicher & Schüll blue-ribbon filter papers from the same lot were used as the filtering medium. The height of the precipitate was nearly constant at 6 mm in all experiments. All filtrates were clear solutions and no thorium was detected upon analysis (sensibility of method: < 1 ppm).

The thorium nitrate solutions were prepared from mantle-grade $Th(NO_3)_4.4H_2O$ supplied by the Administração da Produção da Monazita (APM, São Paulo). Technical grade nitric and oxalic acids were used in the experiments.

3. DESIGNS, DATA AND DISCUSSION

The experimental work had the primary objective of establishing the necessary conditions for obtaining a maximized filtration rate of the oxalate formed by precipitation from a 60g ThO_2/l solution(*) of thorium nitrate. An analysis of the existing literature in this field[1,2,3,4,5,6] indicated that the nature of the precipitate formed from a solution of a given concentration was mainly a function of 4 variables, namely, the precipitation temperature (x_1), the precipitation-digestion time (x_2), the initial free HNO_3 concentration (x_3) and the excess oxalic acid over the stoichiometric amount (x_4). An experimental design was then set up on these variables.

The experimental design consisted of a half-replicate of a 2^4 factorial design, by confounding the fourth variable (excess oxalic acid) with the ternary interaction $x_1x_2x_3$. The main effects were then confounded only with ternary interactions which were expected to be negligible throughout the experimental domain. Table 4.1 shows the effects and interactions that could be supplied by the design.

Table 4.1

Effects and Interactions of the Design

Effects	Interactions
x_1	x_1x_2, x_3x_4
x_2	x_1x_3, x_2x_4
x_3	x_1x_4, x_2x_3
x_4	

* The concentration of 60g ThO_2/l was chosen to coincide with the concentration of the exit stream of the thorium purification process presently in use at the IEA.

The data obtained by this design was the starting point for the Box-Wilson[7] maximization procedure. The problem was to maximize a function of the type.

$$y = y(x_1, x_2, x_3, x_4) \qquad (4.1)$$

where y was the observed filtration rate and the variables x_i were as defined previously. Since in this first design we expected to be far from the optimum conditions, a first degree polynomial on these variables was employed in the calculation of the steepest ascent path. The coefficients were to be evaluated by the usual procedure of least square fitting the data of the orthogonal design[8].

First Design

The levels of the factors employed in the first design are given in Table 4.2. Table 4.3 shows the first design on these factors and the resulting data. Variables x_i are reported in the standardized form

$$x_i = \frac{a_i - \text{base}}{\text{unit}} \qquad (4.2)$$

Least square fitting the data in Table 4.3 resulted in the coefficients of Table 4.4 for the regression polynomial, along with the interactions of Table 4.1.

Table 4.2

Levels of the factors in the first design

Factor	Level −	Level +	Base Level	Unit
a_1 temperature, °C	15	30	22.5	7.5
a_2 time, min.	10	30	20	10
a_3 initial HNO_3 conc., N	0	2	1	1
a_4 excess oxalic acid, %	5	20	12.5	7.5

Table 4.3

First design and data

Run	x_1	x_2	x_3	x_4	yobs. (ml/min)
1	-1	-1	-1	-1	38.8
2	+1	-1	-1	+1	125.7
3	-1	+1	-1	+1	22.5
4	+1	+1	-1	-1	113.2
5	-1	-1	+1	+1	446.4
6	+1	-1	+1	-1	381.7
7	-1	+1	+1	-1	410.4
8	+1	+1	+1	+1	574.2

Defining contrasts: 1, $x_1x_2x_3x_4$

Table 4.4

Coefficients of the regression polynomial in the first design

b_o	= 264.1	$\pm$ 15
b_1	= 34.6	$\pm$ 15
b_2	= 16.0	$\pm$ 15
b_3	= 189.1	$\pm$ 15
b_4	= 28.1	$\pm$ 15
$b_{12,34}$ (x_1x_2, x_3x_4)	= 29.0	$\pm$ 15
$b_{13,24}$ (x_1x_3, x_2x_4)	= - 9.8	$\pm$ 15
$b_{14,23}$ (x_1x_4, x_2x_3)	= 23.2	$\pm$ 15

The terms within parentheses serve to remind that the calculated coefficients are a measure of those interactions. The error was calculated from an independent determination of the experimental error variance, $s^2 = 1800$.

An analysis of Table 4.4 indicates that the center of

the design is located in a region subject to appreciable binary interactions. Two-way interaction tables constructed with the data on Table 4.3, indicated that the higher levels favored all interactions in the system. On the other hand the coefficients of the main effects indicated the need for increasing all levels with respect to the base. The steepest gradient was that along the axis x_3, followed in order of importance by x_1 and x_4, and a small slope along axis x_2.

The calculation of the steepest ascent path was performed with these coefficients in increments of 0.5 in variable a_3, as shown in Table 4.5. Observed and calculated values for y are also reported. There was poor agreement between these values at all points. The ever increasing values of the calculated y given by the linear polynomial could not detect the curvature of the experimental response surface around the value 3.0N in variable x_3. Nevertheless, the observed value of y indicated a conditional maximum, and the decision was made to set up a new design around this point.

Second Design

The second design was centered around the value of variable x_3 at the maximum in the steepest ascent path of the first design, but the base levels of all other variables were displaced to higher values and the units decreased, in order that the interactions could be favored and the importance of variable x_2 could be evaluated. The levels of the variables in the second design are given in Table 4.6. The design and the data are given in Table 4.7. The rates obtained were now in all cases higher than the maximum value obtained in the path of ascent of the first design.

Least square fitting the data in Table 4.7, again with a first order regression polynomial, resulted in the coefficients reported in Table 4.8, along with the interaction pairs. The analysis of these coefficients shows that only the temperature is important in this region of experimentation, there being also

little influence of the excess oxalic acid and appreciable interaction measured by $b_{14,23}$. Two-way interaction tables constructed for the interactions x_1x_4 and x_2x_3, indicated that the former was the most important interaction. The coefficients also indicated that we had crossed over a maximum and most of the variables had to be decreased with respect to the base level to attain even higher rates. Since the interactions between the variables were now all small, a new path of ascent was calculated employing again a first order polynomial. This data are reported and observed y's are also given for points along the path. The agreement between the y's were now much better up to the maximum in the observed rate. It was decided then that a satisfactory rate had been attained and no further effort was made to determine if this was only a local maximum, or an absolute maximum in the experimental domain.

Table 4.5

Path of Steepest Ascent for the first design

Steepest ascent path				y calculated (ml/min)	y observed (ml/min)
a_1 (^oC)	a_2 (min)	a_3 (N)	a_4 (%)		
22.5	20.0	1.0	12.5	264.1	---
23.2	20.4	1.5	13.1		
23.9	20.8	2.0	13.7	465.4	415.9
24.6	21.2	2.5	14.3		
25.3	21.6	3.0	14.9	666.6	457.9
26.0	22.0	3.5	15.5		
26.7	22.4	4.0	16.1	868.1	397.2

Table 4.6

Levels of the factors in the second design

Factor	Level −	Level +	Base Level	Unit
a_1 temperature, ^{o}C	30	40	35	5
a_2 time, min.	25	35	30	5
a_3 initial HNO_3 conc., N	2.5	3.5	3	0.5
a_4 excess oxalic acid, %	15	25	20	5

Table 4.7

Second design and data

Run	x_1	x_2	x_3	x_4	$y_{obs.}$ (ml/min)
1	-1	-1	-1	-1	681.8
2	+1	-1	-1	+1	961.5
3	-1	+1	-1	+1	524.5
4	+1	+1	-1	-1	833.3
5	-1	-1	+1	+1	483.9
6	+1	-1	+1	-1	862.1
7	-1	+1	+1	-1	641.0
8	+1	+1	+1	+1	872.1

Defining contrasts: $1, x_1x_2x_3x_4$

Table 4.8

Coefficients of the regression polynomial of the second design

b_o	=	732.5	± 15
b_1	=	149.7	± 15
b_2	=	-14.8	± 15
b_3	=	-17.8	± 15
b_4	=	-22.0	± 15
$b_{12,34}$ (x_1x_2, x_3x_4)	=	-14.8	± 15
$b_{13,24}$ (x_1x_3, x_2x_4)	=	2.6	± 15
$b_{14,23}$ (x_1x_4, x_2x_3)	=	56.6	± 15

To further verify the effects of the individual variables upon the rate of filtration, and to ascertain whether there was a rising ridge in the vicinity of the observed maximum, the parametric variation of the factors was made by the usual one-at-time variable change. The resulting data are plotted in Figs. 1 through 4 and represent sections of the 4-variable response surface along the axes of the variables. This procedure serves as a check on the validity of the conclusions obtained from the path of ascent given by the fitting polynomial. Furthermore the maxima in all curves should not exceed the maximum in the steepest ascent path and the levels corresponding to the maxima in these curves should coincide with the levels specified in the maximum in the path of ascent, in the absence of a rising ridge. This is indeed the case, as indicated in these figures except for the excess oxalic acid which was somewhat understimated (Fig. 4). If a rising ridge was obtained, additional experimentation would be needed, which was not fortunately the case. From the analysis of the curves it was then concluded that for a 60 g ThO_2/l solution of thorium nitrate a maximum in the filtration rate of the oxalate occurs around the point

precipitation temperature:	60 $\pm$ 4° C
precipitation-digestion time:	28 $\pm$ 2 min
initial free HNO_3 concentration:	3.1 $\pm$ 0.3N
excess oxalic acid:	20 $\pm$ 3 %

Table 4.9

Path of Steepest Ascent for the second desing

Steepest ascent path				y calculated (ml/min)	y observed (ml/min)
a_1 (°C)	a_2 (min)	a_3 (N)	a_4 (%)		
35	30.0	3.00	20.0	732.2	---
40	29.5	2.94	19.3	889.0	781.3
45	29.0	2.88	18.5		
50	28.5	2.82	17.8	1202.0	1327.5
55	28.0	2.76	17.0		
60	27.5	2.71	16.3	1514.5	1503.0
65	27.0	2.65	15.6		
70	26.5	2.59	14.8	1838.3	1271.2

The oxalate formed under these conditions is a non--hygroscopic, almost free-flowing crystalline powder with the formula $Th(C_2O_4)_2.6H_2O$. A microscope photograph of a sample of this oxalate is shown in Fig. 5. The photograph shows a range of particle sizes from 0.5μ amorphous particles to 4μ well-defined quadratic prisms.

In order to investigate the applicability of the conclusions drawn above to solutions of concentrations other than 60g ThO_2/l, solutions containing 40 and 80g ThO_2/l were precipitated under the optimized conditions for the 60g ThO_2/l solution, and parametric variation of the initial HNO_3 concentration was made.

The results are shown in Fig. 6. This figure indicates that optimization must be effected for each particular concentration level of the thorium nitrate solution. The conclusions then herein stated are only applicable to a 60g ThO_2/l thorium nitrate solution.

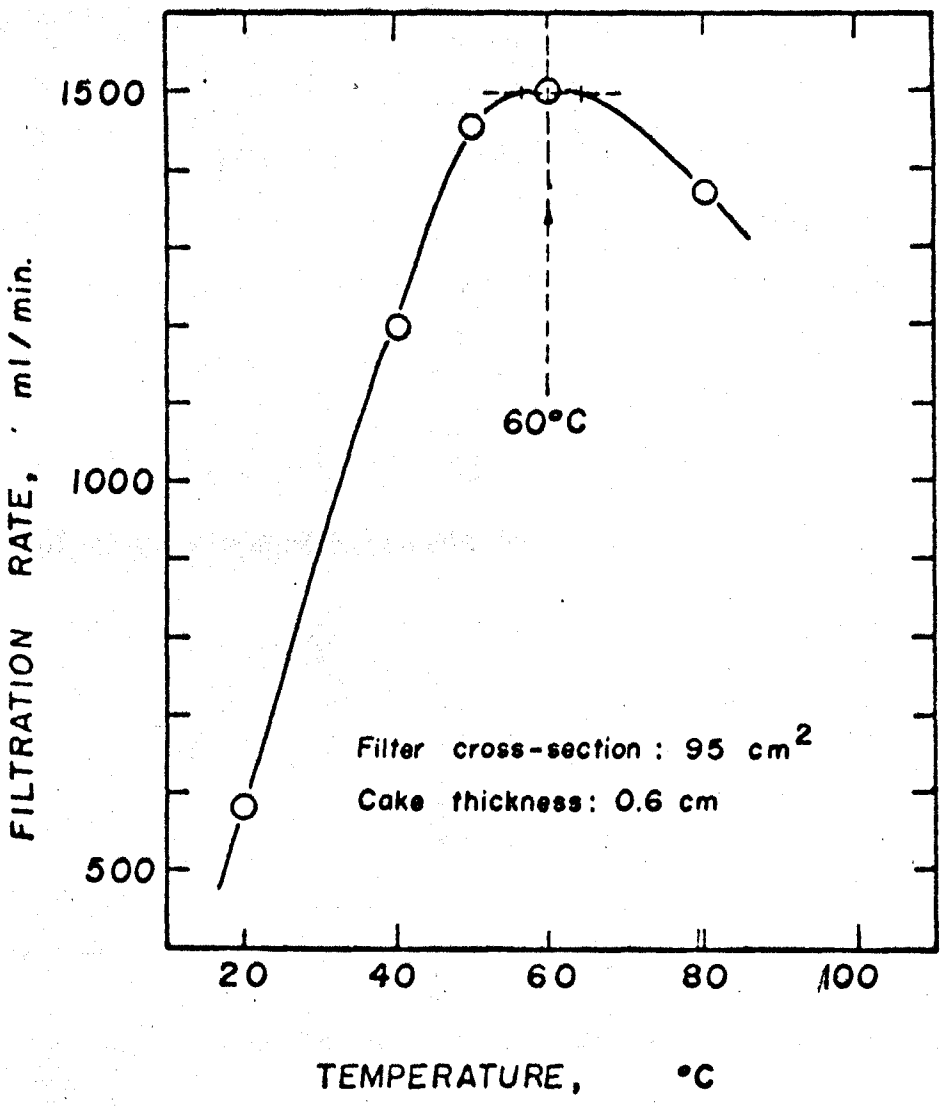

Fig. 1 Filtration Rate vs. Temperature

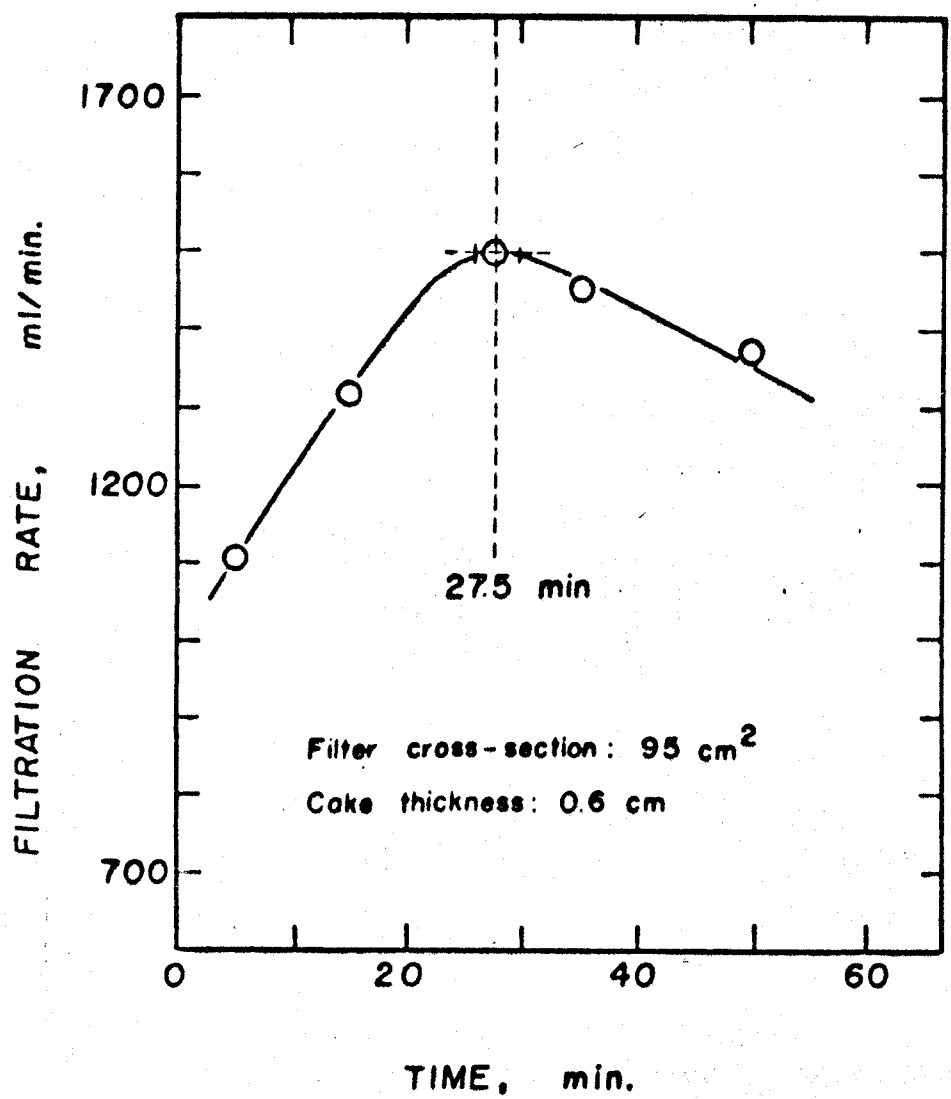

Fig. 2 Filtration Rate vs. Time

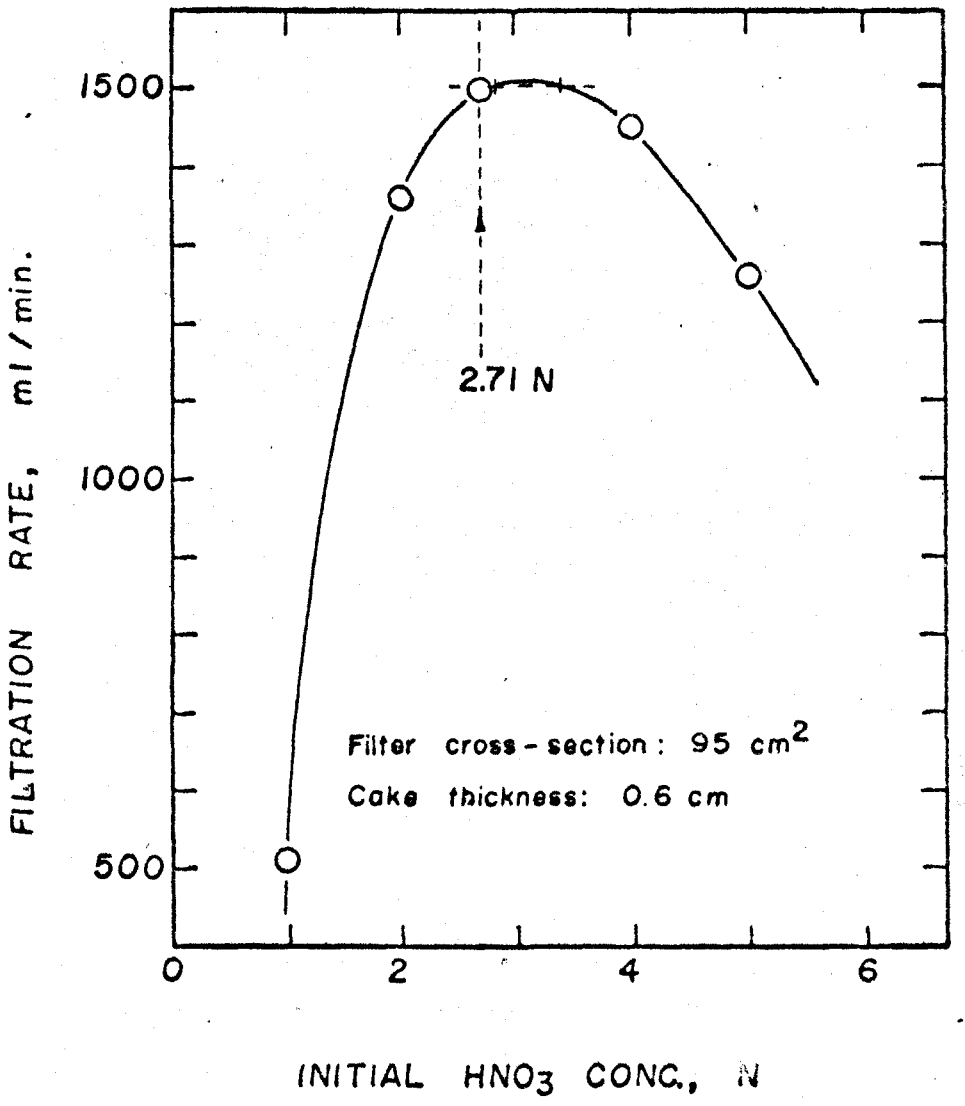

Fig. 3 Filtration Rate vs. Initial HNO_3 Conc.

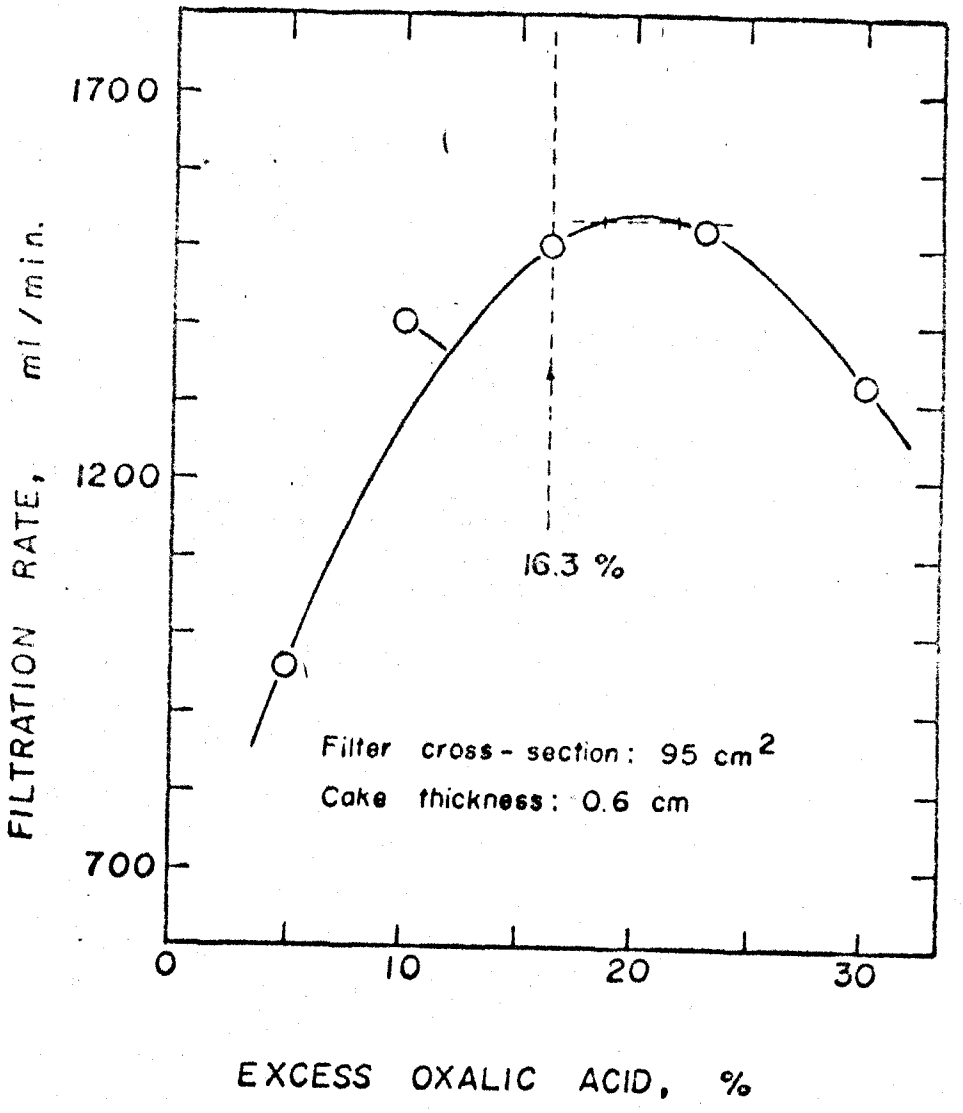

Fig. 4 Filtration Rate vs. Excess Oxalic Acid

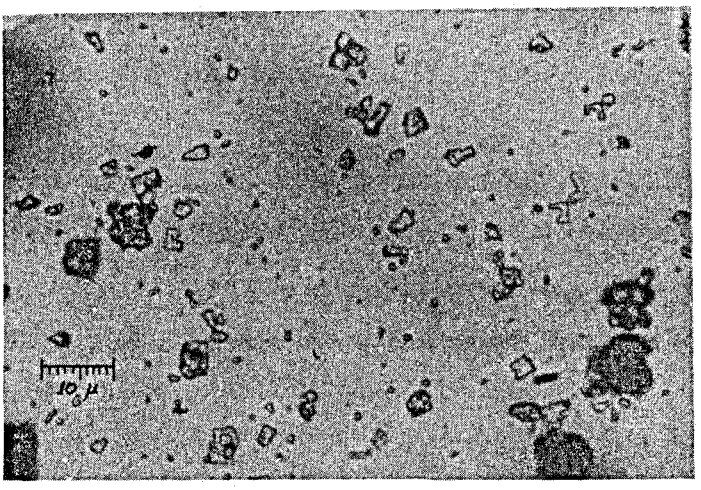

Fig. 5 - Thorium oxalate precipitated under optimized conditions.

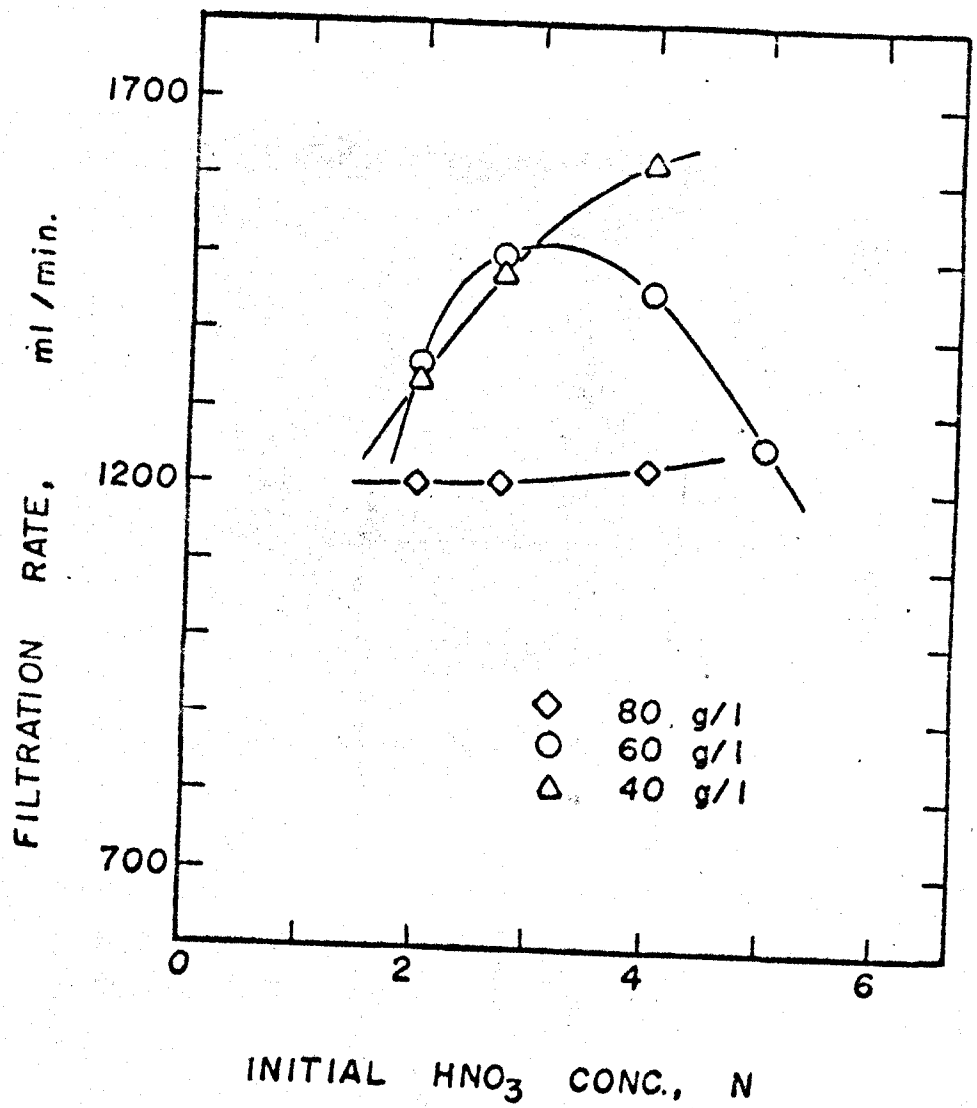

Fig. 6 Filtration Rate vs. Initial HNO_3 Conc.

4. CONCLUSIONS

The main conclusions drawn from this study were as follows.

1 - The optimization of the precipitation conditions of thorium oxalate can be carried out by a steepest ascent procedure using the filtration rate as the response variable.

2 - For a 60g ThO_2/l thorium nitrate solution a maximized filtration rate is obtained around the point 60 ± 4^oC, 28 ± 2 min, $3.1 \pm 0.3N$ HNO_3, $20 \pm 3\%$ excess oxalic acid.

3 - The main interaction near the optimum response is that between the precipitation temperature, x_1, and the excess oxalic acid, x_4.

4 - The optimization conditions herein stated are only valid for a 60g ThO_2/l thorium nitrate solution. A solution of any other concentration in the range 40 to 80g ThO_2/l seems to yield a lower filtration rate at these conditions.

RESUMÉ

On a étudié la maximization de l'effet de 4 variables (le temps, la température, la concentration de l'HNO_3 et l'excès d'acide oxalique) sur le taux de filtration d'un oxalate de thorium hexahydraté, precipité d'une solution de $Th(NO_3)_4$ contenant 60g ThO_2/l. Les précipitations ont été effectuées dans un réacteur discontinu, agité, en échelle de laboratoire, pour donner une quantité constante de $Th(C_2O_4)_2.6H_2O$ chaque fois, tandis que dans l'etape de filtration un volume constant de solution a été filtré dans le vide, en employant des papiers à filtrer d'un même lot.

L'optimization a été effectuée par la Méthode d'Ascension Rapide employant des données experimentaux provenant d'une programmation factorielle fractionnée 2^3 en 4 variables. Ont été necessaires 25 expériences. Pour une solution contenant 60g ThO_2/l, on obtient un maximum dans le taux de filtration par précipitation d'une solution $3.1 \pm 0.3N$ en HNO_3 à ... 60 ± 4^oC, en employant 20 - 3% d'excès d'acide oxalique et un temps de précipitation-digestion de 28 ± 2 min. La vérification de ces données a été effectuée par la variation individuelle de variables autour de ce point. Des solutions contenant 40 et 80g ThO_2/l on été aussi étudiées dans ces mêmes conditions, mais des résultats ont indiqué la necessité d'optimization pour chaque concentration de nitrate de thorium choisie.

RESUMO

A maximização do efeito de 4 variáveis (tempo, temperatura, concentração inicial de HNO_3 e excesso de ácido oxálico) sôbre a velocidade de filtração de um oxalato de tório hexa hidratado, precipitado de uma solução de $Th(NO_3)_4$ contendo 60g ThO_2/l, foi estudada. As precipitações foram realizadas em um reator descontínuo, agitado, em escala de laboratório, a pêso constante de $Th(C_2O_4)_2.6H_2O$, enquanto que na etapa de filtração um volume constante de solução foi filtrado sob vácuo constante, utilizando-se papéis de filtro de um mesmo lote.

A optimização foi efetuada pelo Método de Ascenção Rápida, empregando-se dados experimentais obtidos com meio bloco de uma programação fatorial 2^4. Um total de 25 testes foram necessários. A análise dos dados indicou que a velocidade máxima de filtração para uma solução de 60g ThO_2/l é obtida pela precipitação a 60 ± 4°C de uma solução 3.1 ± 0.3N em ... HNO_3, usando 20 ± 3% de ácido oxálico em excesso com um tempo de precipitação-digestão de 28 ± 2 min. A verificação dêstes dados foi feita pela variação paramétrica individual em tôrno do máximo. Soluções contendo 40 e 80g ThO_2/l foram também precipitadas nestas condições, contudo, os resultados indicaram a necessidade de optimização para cada nível de concentração do soluto escolhido.

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