REMOVAL OF FISSION PRODUCT RUTHENIUM FROM PUREX PROCESS SOLUTIONS: THIOUREA AS COMPLEXING AGENT

Bertha Floh and Alcídio Abrão

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INIS Categories and Descriptors

B16

URANIUM: Reprocessing
SPENT FUELS: Reprocessing
SPENT FUELS: Purex process
RUTHENIUM: Complexometry
RUTHENIUM: Decontamination

REMOVAL OF FISSION PRODUCT RUTHENIUM FROM PUREX PROCESS SOLUTIONS: THIOUREA AS COMPLEXING AGENT*

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ABSTRACT

A new method for the treatment of spent uranium fuel is presented. It is based on the Purex Process using thiourea to increase the ruthenium decontamination factor.

Thiourea exhibits a strong tendency for the formation of coordination compounds in acidic media. This tendency serves as a basis to transform nitrosyl-ruthenium species into $Ru \mid SC(NH)(NH_2) \mid^{2+}$ and $Ru \mid SC(NH)(NH_2) \mid_3$ complexes which are unextractable by TBP-varsol. The best conditions for the ruthenium-thiourea complex formation were found to be: thiourea-ruthenium ratio (mass/mass) close to 42, at $75^\circ C$, 30 minutes reaction time and aging period of 60 minutes. The ruthenium decontamination factor for a single uranium extraction are ca. 80-100, not interfering with extraction of actinides. These values are rather high in comparison to those obtained using the conventional Purex Process (e.g. $F.D._{(Ru)} = 10$). By this reason the method developed here is suitable for the treatment of spent uranium fuels.

Thiourea (100 g/ℓ) scrubbing experiments of ruthenium, partially co-extracted with actinides, confirmed the possibility of its removal from the extract. A decontamination greater than 83,5% for ruthenium as fission product is obtained in two stages with this procedure.

In the development of solvent extraction flowsheets for the separation of fission products from fertile and fissile materials, it is invariably found that some of the fission products are more troublesome than others. Ruthenium and zirconium-niobium are the main contaminants that remain in the solution of recovered uranium after one purification cycle by the Purex Process. Such solutions contains trivalent nitrosyl-ruthenium complexes in which the ligands are nitrato, nitro, hydroxo and aquo groups[3], easily converted into each other and that co-exist in the feed solution.

Much work is done to unravel the complex chemistry of the nitrosyl-ruthenium compounds[2,7,8]. A starting point in the research work on these compounds is always the trinitrato of nitrosyl-ruthenium, $RuNO (NO_3)_3 (H_2O)_2 . 2 H_2O$. By some techniques like paper chromatography, ion exchange, solvent extraction and complexation it was proved that TBP extracts ruthenium by forming $RuNO (NO_3)_3 . 2 TBP$ complexes[1,5,6]. As a general approach it can be said that as more nitrato groups are present in the molecule, the better the compound is extracted by TBP, while the nitro-compound is relatively unextractable[4].

The present work describes investigations concerning the influence of thiourea as complexing agent on the extraction behaviour of ruthenium from sinthetic feed solutions.

2

Experimental

    — Reagents:

(A) Nitrosyl-ruthenium stock solution: $10^{-3} - 10^{-2}$M Ru, labelled with ^{106}Ru $- ^{106}$Rh in 7M HNO_3 medium; prepared according to Fletcher[3]. 10^{-4}M Ru solutions obtained by dilution of (A) and agged for at least two weeks to achieve equilibrium between the complexes.

Uranyl nitrate — prepared by dissolution of nuclear grade uranium oxide, obtained from the Uranium Pilot Plant, Chemical Engineering Center, IEA.

    — Extractant:

TBP-Varsol, a paraffinic naphta, supplied by Esso Standard do Brasil, containing approximately 18% of aromatic hydrocarbons. All the organic solutions were pre-equilibrated with HNO_3 at the same acidity of the feed solutions.

Extraction Data

In the early stages of the extraction process development, it was thought that a large amount of information could be gained if the experimental data were sucessively taken, from one-component to multi-component solutions. In order to achieve those results it was checked some influences (e. g. free acid, organic loading, O/A) on the nitrosyl-ruthenium extraction behaviour. All reported data was taken at room temperature (25°C).

From a 30% TBP-varsol solution the distribution coefficient of ruthenium decrease with increasing aqueous nitric acid concentration from 0.1 to 5M (Figure 1). Distribution of ruthenium between the TBP and aqueous phases is governed by a series of kinetic reactions both within and between the phases. With a 3.5×10^{-4}M Ru in 0.25M HNO_3 solution it was found that equilibrium is established after 100 minutes (Figure 2). It appears that on short residence time contactors ruthenium decontamination factor $DF_{(Ru)}$ will increase.

The distribution coefficients for ruthenium $D_{(Ru)}$ decrease with increasing uranium concentration in the organic phase. At the uranium saturation range $10 - 70\%$, it was found that $D_{(Ru)}$ values diminish from 0.8 to 0.2 (Figure 3).

At high TBP concentration in the organic phase better is the extraction of ruthenium (Figure 4). The same effect is observed at higher O/A ratio. The extraction increase from 10 to 40% as O/A varied from 10 to 0.1.

Experiments with thiourea solutions (100 g/l) in 0.01M HNO_3 as scrubbing agent has shown that 83.5% ruthenium is removed, in two stages from a TBP-varsol-RuNO $(NO_3)_3 - UO_2(NO_3)_2$ phase.

Complexing and Distribution Behaviour

Variation of thiourea amount was shown (Figure 5) that maximum ruthenium decontamination is obtained with increasing thiourea/Ru ratio. At a maximum ratio of 1000 the ruthenium distribution coefficient decreases from 0.9 to 0.3. Nevertheless at a ratio higher than 56 the organic phase becames cloudy. The experiments were carried out at room temperature (25°C) with one hour reaction time.

Temperature effect on the complexing reaction has been studied. With a 0.25M $HNO_3 - 5M$ $NaNO_3$ solution, (thiourea/Ru) $= 42$, it has been found that after 1 hour reaction time, $70 - 80°$C is

the best temperature range to allow the minimum ruthenium extraction (Figure 6). Those blue — greenish complexes corresponds probably to the formulas $Ru |SC(NH)(NH_2)|^{2+}$ and $Ru |SC(NH)(NH_2)|_3$.

The best results to improve ruthenium decontamination were achieved when the reaction time was higher than 30 minutes, at $75°C$. In such conditions, under agitation, the $D_{(Ru)}$ is 0.02 (Figure 7). This values decreases to 0.01, or less, after agging the ruthenium-thiourea solution before extraction.

Complexing of ruthenium with thiourea has no influence on uranium extraction from a 3M HNO_3 solution. Several experiments are shown that the losses are less than 1%, increasing from 0.1 to 0,9% as the uranium concentration increase in the aqueous phase from 10 to 80 g/l, for one stage and $O/A = 1$. The complexation of ruthenium with thiourea in a synthetic (3M HNO_3) feed solution before the uranium (80 g U/l) extraction with 30% TBP-varsol 15 minutes extraction time, $O/A = 1$, gives a $DF_{(Ru)}$ reaching 100.

Conclusion

From the results above described, the following conclusions can be drawn:

1) Thiourea improves ruthenium decontamination in the uranium extraction with TBP-varsol.

2) The best conditions for the complexing reaction are: Thiourea/ruthenium = 42, at $75°C$, reaction time 30 minutes, agging 1 hour before uranium extraction.

3) The blue-greenish complexes obtained probably have the formulas: $Ru |SC(NH)(NH_2)|^{2+}$ and $Ru |SC(NH)(NH_2)|_3$, described by Yaffe & Voight[9].

4) The complexation of ruthenium with thiourea has no marked influence on the uranium extraction by TBP. The maximum uranium loss is about 0.9%, when uranium is extracted with 30% TBP-varsol from a 80 g U/l, 3M in HNO_3; in such conditions $DF_{(Ru)}$ were 80 -- 100.

RESUMO

Apresenta-se um novo método para o tratamento de combustíveis de urânio irradiado. O método, baseado no processo purex, usa tiouréia para aumentar a descontaminação do rutênio.

Tiouréia em meio ácido mostra forte tendência à formação de compostos por coordenação. Esta característica serviu de fundamento para se transformar as espécies de nitrosil-rutênio em complexos $Ru |SC(NH)(NH_2)|^{2+}$ e $Ru |SC(NH)(NH_2)|_3$, não extraídos por TBP-varsol. As condições ideais para a formação dos complexos rutênio-tiouréia são: relação tiouréia-rutênio (massa/massa) próxima de 42, $75°C$ em 30 minutos e envelhecimento de 60 minutos. Os fatores de descontaminação do rutênio, para um único estágio de extração do urânio, são da ordem de 80-100. Estes valores elevados, comparados com os obtidos nos esquemas fundamentais do processo Purex (F.D.$_{(Ru)}$ $\approx$ 10), indicam que o método é eficiente, simples e de baixo custo, além de não interferir com a extração dos actinídios.

Experimentos de reversão do rutênio, parcialmente coextraído com os actinídios, com tiouréia 100 g/ℓ, indicaram a possibilidade de sua remoção. Neste procedimento obtém-se, em dois estágios de reversão, uma descontaminação de pouco mais de 83,5% do produto de fissão rutênio.
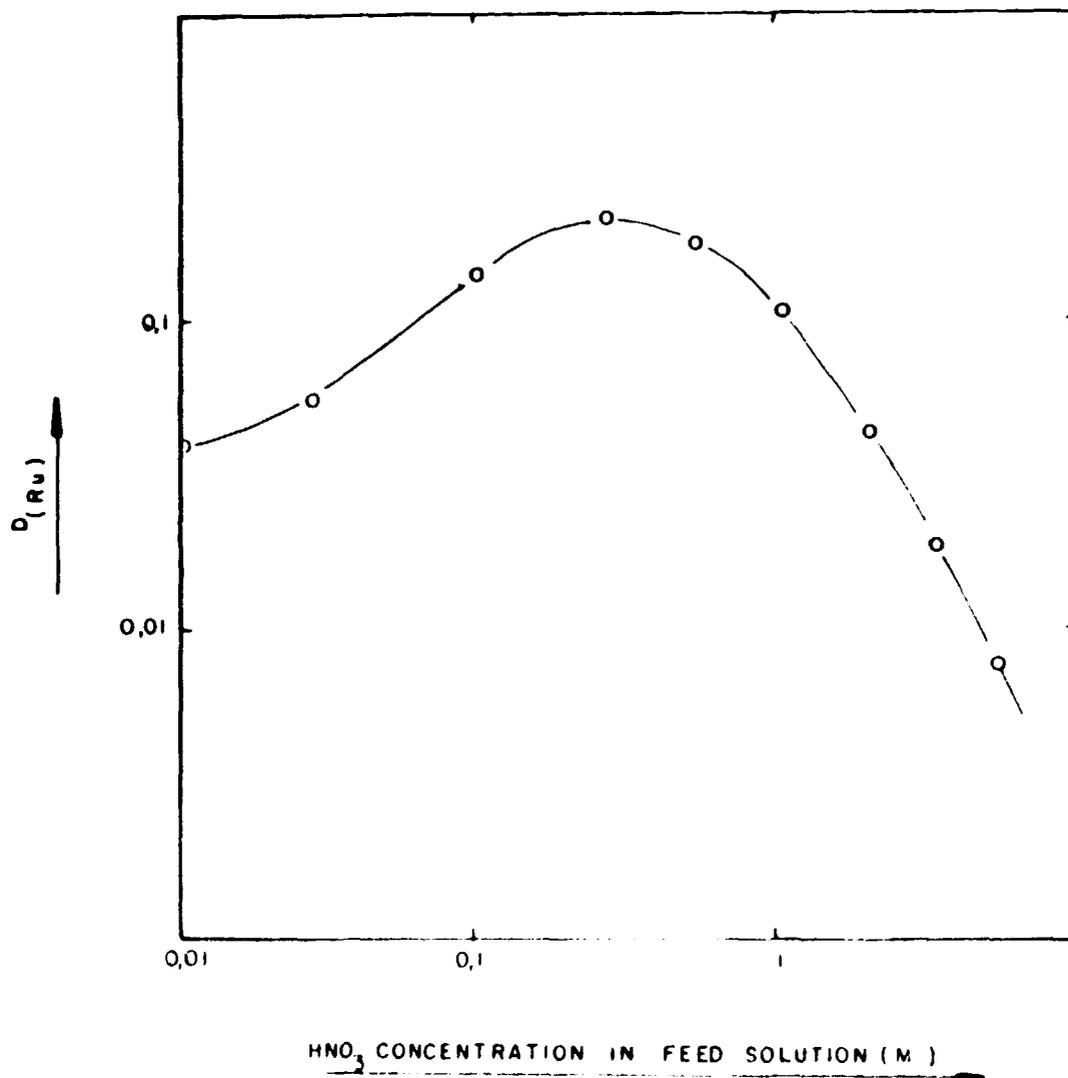
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Figure 1   HNO$_3$ effect in the feed solution. $|Ru|_a$ = 3,5 x 10^{-4} M. TBP = 30%. O/A = 1.T = 25°C.
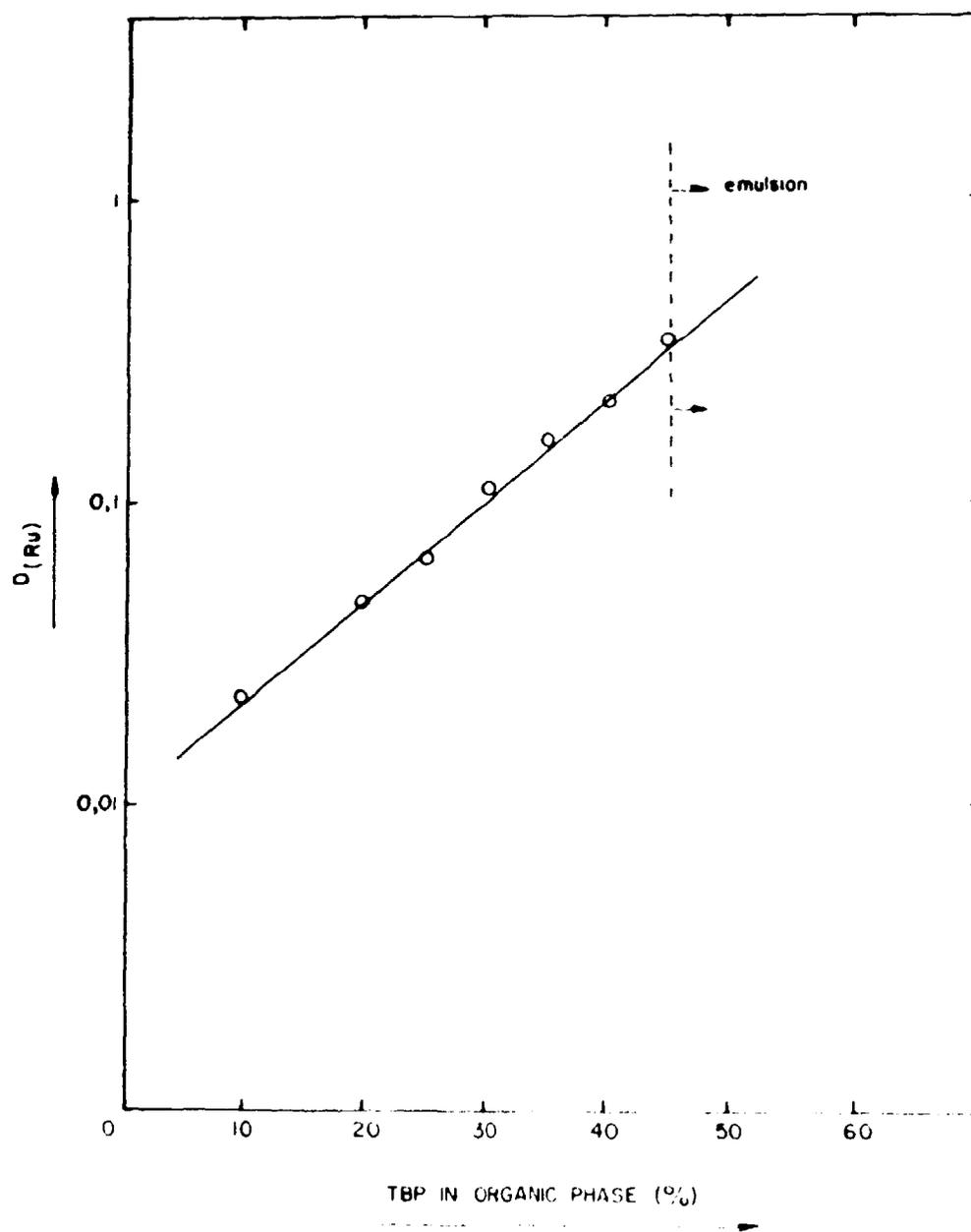t = 1 min . v = 2500 rpm

Figure 2 — Influence of TBP concentration on $RuNO^{3+}$ extraction. $|Ru|_a = 3.5 \times 10^{-4}$ M . $|H|_a$ = 0.25 M. O/A = 1 T = 25°C. t = min, v = 2500 rpm
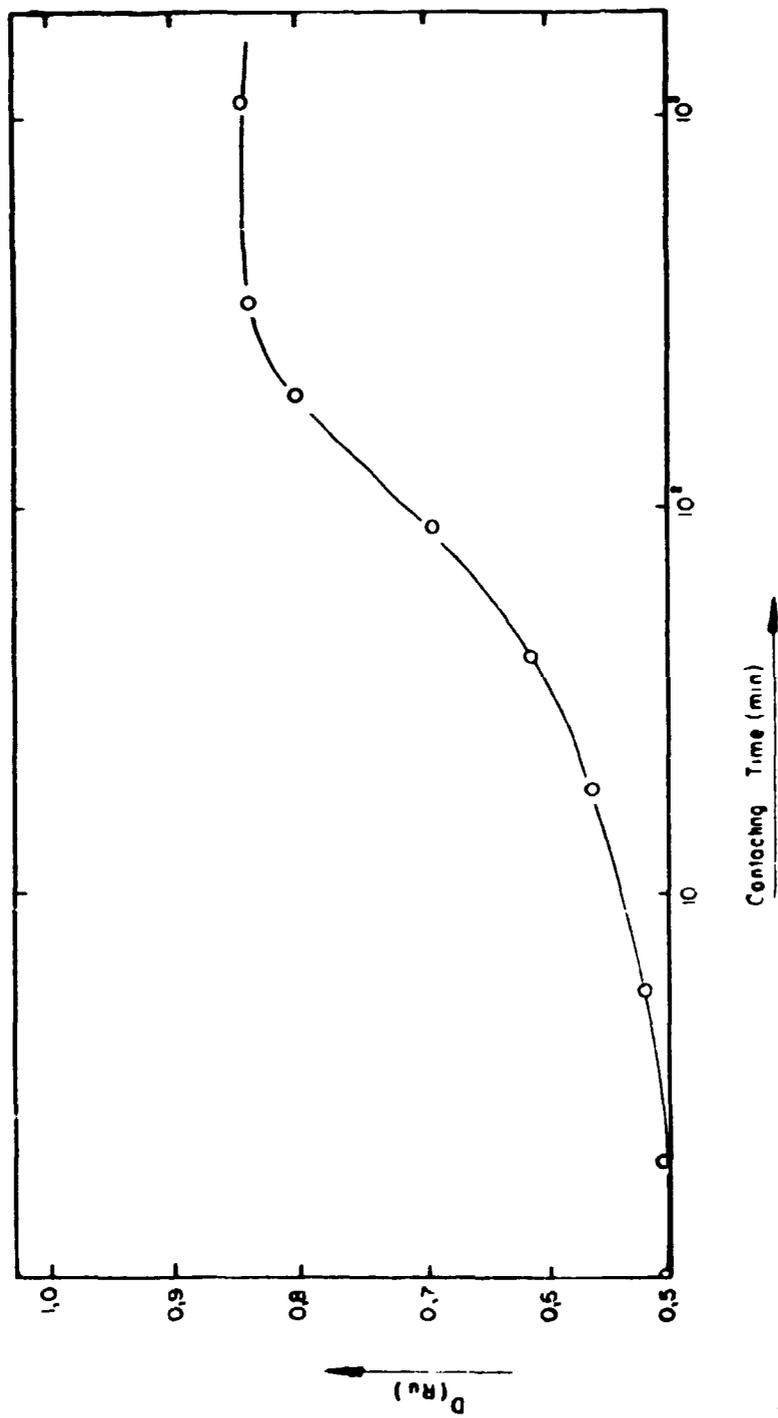
Figure 3 — Contact time effect on Ru extraction with TBP-varsol, $|Ru|_d$ = 3.5 x 10^{-4} M, $|H|_a$ = 0,25 M, TBP = 40%, O/A = 1, T = 25°C, v = 2500 rpm
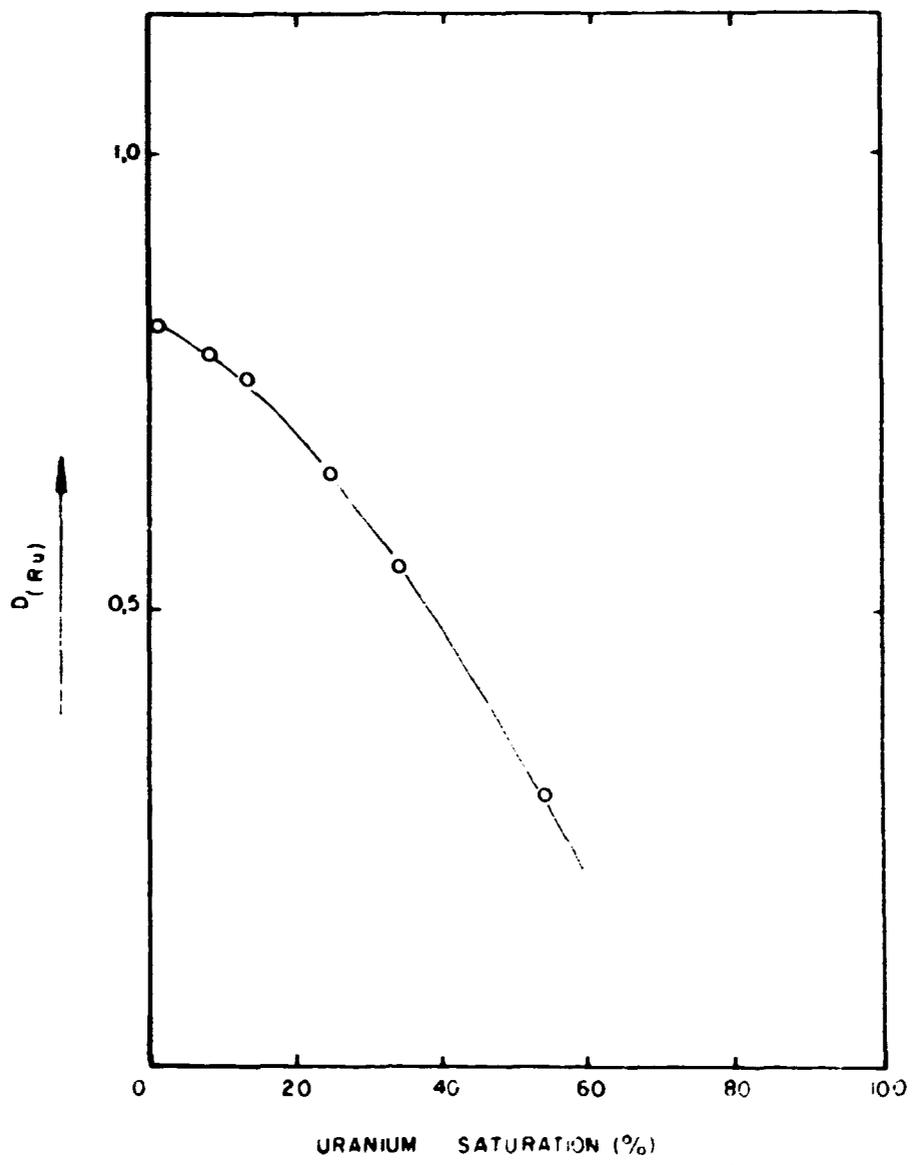
Figure 4 – Uranium saturation effect on ruthenium extraction with TBP-varsol. IRu; 3.5 x 10⁻¹ M. IHI; 0.25 M. TBP - 40%. O/A = 1. T - 25° v 2500 rpm.
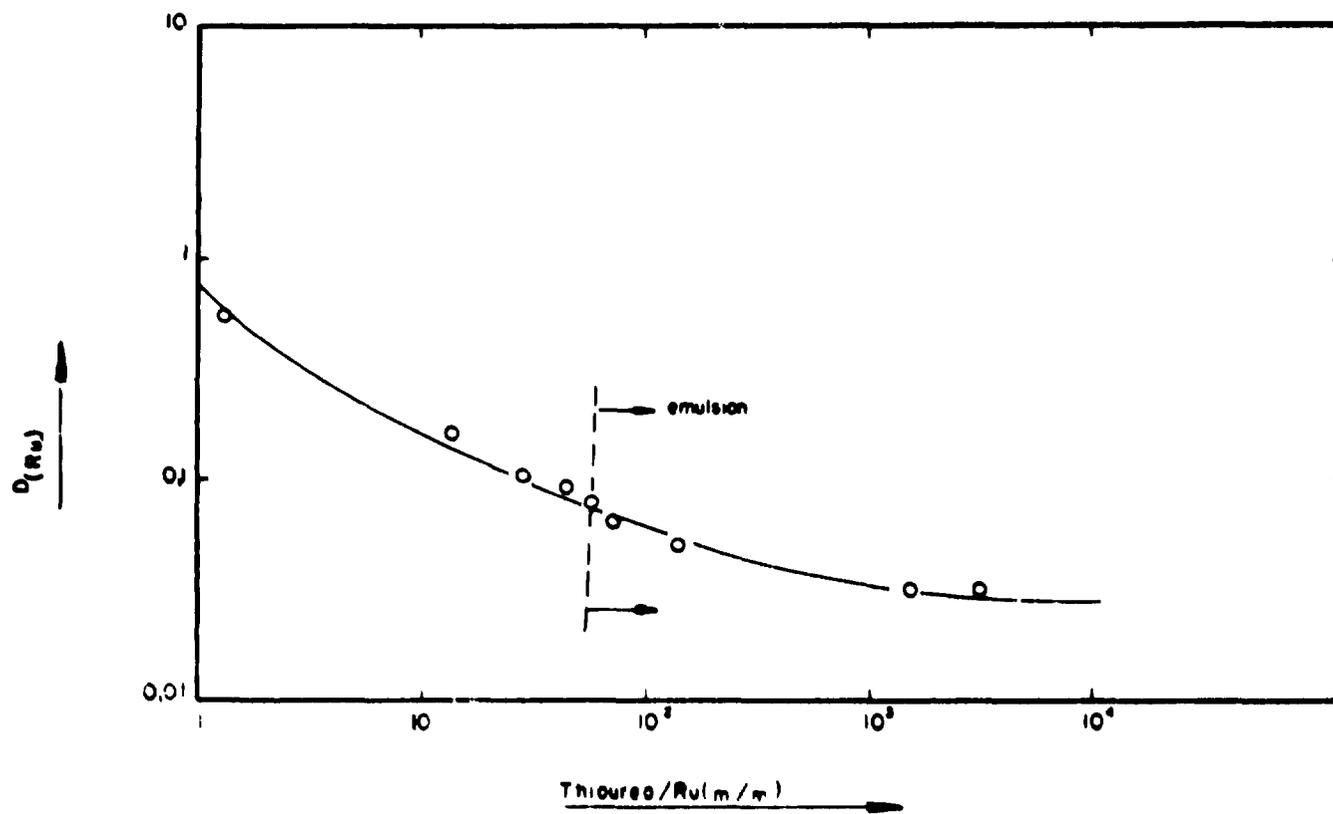
Figure 5 — Thiourea/Ruthenium effect on complexation and extraction of ruthenium with TBP-varsol, $t_c = 1$ h, T = 25°C, v = 2500 rpm
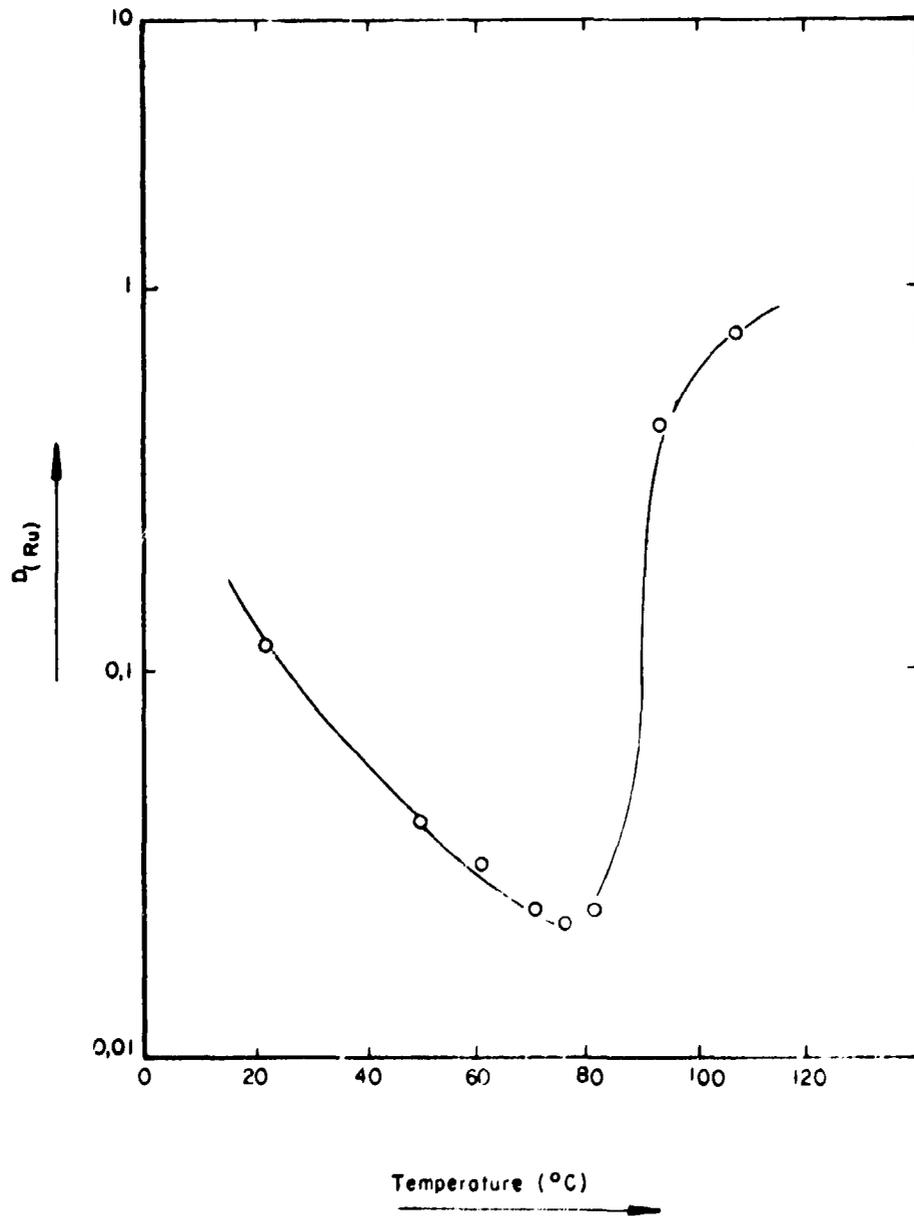
Figure 6 — Temperature effect on the ruthenium complexation and extraction with TBP-varsol, t_c = 1 h. v = 2500 rpm

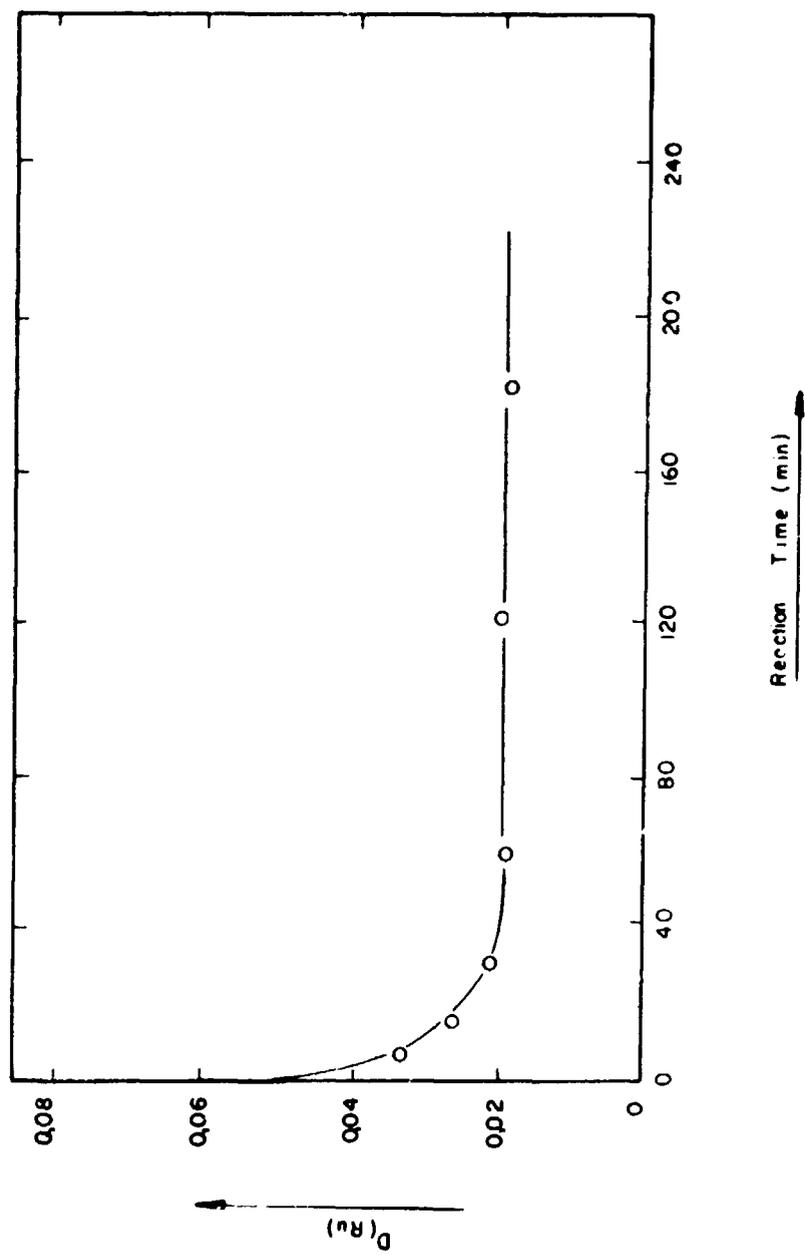Figure 7 — Effect of reaction time on Ru/Thiourea complexation and extraction with TBP. T = 75°C. v = 2500 rpm

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