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CALCULATED AND EXPERIMENTAL STUDIES OF NON-EQUILIBRIUM SOLVENT EXTRACTION OF URANIUM-THORIUM AND URANIUM-ZIRCONIUM*

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ABSTRACT

The non-equilibrium simultaneous transfer of ions in solvent extraction has been examined experimentally and these results have been compared with the calculated behavior determined using transfer rate constants. In the Th-U system when transferring from 2 $\underline{M}$ HNO_3 into 30% tributyl phosphate (TBP) in normal hydrocarbon diluent (NPH), the thorium approaches equilibrium faster than uranium over much of the transfer region. Thus, non-equilibrium operation will not increase the separation factor between uranium and thorium over that attained at equilibrium. However, in the Zr-U system when transferring from 3.4 $\underline{M}$ HNO_3 into 30% TBP-NPH, the separation factor between uranium and zirconium is increased over that attained at equilibrium over much of the transfer region due to the relatively slow transfer of $ZrOH^{3+}$, one of the two extractable forms of zirconium. Thus, the uranium-zirconium separation factor can potentially be increased by the use of short, non-equilibrium residence times.

INTRODUCTION

The Purex process and the similar Thorex process are accepted processes for reprocessing spent reactor fuels. In these processes the desired materials (uranium, plutonium, and thorium) are extracted by tributyl phosphate dissolved in a hydrocarbon diluent and are separated from the bulk of the fission products which remain in the nitric acid solution. Contactors for the process include near-equilibrium contactors such as mixer-settlers, differential contactors such as pulse columns, and short-time contactors such as centrifugal contactors. For each contactor it would be valuable to know how the approach to equilibrium varies for each element. For instance, it is conceivable that, by a proper choice of operating conditions, the extraction of fission products can be minimized if their transfer rates are significantly lower than those of the actinides of interest.

Over the past several years we have determined the interphase transfer kinetics of uranium,[1] thorium,[2] and zirconium.[3] Using the rate constants determined in these studies, the approach to equilibrium can be predicted for these elements. The calculated transfer behavior for uranium-thorium and uranium-zirconium are compared with data from experimental non-equilibrium tests in this paper.

EXPERIMENTAL

Materials

The aqueous solution for the uranium-thorium experiment was prepared by dissolving reprecipitated $Th(NO_3)_4 \cdot 4H_2O$ and $UO_2(NO_3) \cdot 6H_2O$ in nitric acid

to yield a solution containing 0.78 g of uranium and 9.82 g of thorium per liter in 2 $\underline{M}$ HNO_3. The auqeous solution for the uranium-zirconium experiment used a zirconium stock prepared and used in the work described in Ref. [3]. This standard solution contained 0.096 $\underline{M}$ Zr in 3.3 $\underline{M}$ HNO_3 and had been extracted and back-stripped to eliminate inextractable species which are not in equilibrium with extractable species. Uranyl nitrate hexahydrate was weighed out and added to a portion of this solution to yield a final solution containing 9.7 g of uranium per liter; the zirconium and acid remained essentially unchanged. The tributyl phosphate (TBP)--normal paraffin hydrocarbon (NPH) solutions were prepared by diluing TBP with NPH (both obtained from the Savannah River Plant, Aiken, S.C.) and then purifying the solution from possible TBP degradation products by scrubbing twice with sodium carbonate solution, followed by multiple water washes.

Apparatus and procedure

The aqueous and organic phases (60 ml each) were contacted in the apparatus shown in Fig. 1. The organic phase was pre-equilibrated with an aqueous phase of the same HNO_3 content as the aqueous in the experiment. The aqueous phase was added first and then the organic was added slowly by pouring down a glass rod to assure that very little transfer would occur prior to starting the mixer. The mixer was rotated at a speed sufficient to intimately mix the aqueous phase and a portion of the organic phase while leaving a clear organic layer on top. Three or four samples of the clear organic phase were taken over about a 60-sec time period. It is assumed that the concentration of metals in the clear portion of the organic phase is approximately the same as that in the organic containing dispersed

CLEAR ORGANIC

AQUEOUS-ORGANIC
DISPERSION

PERFORATED
MIXER
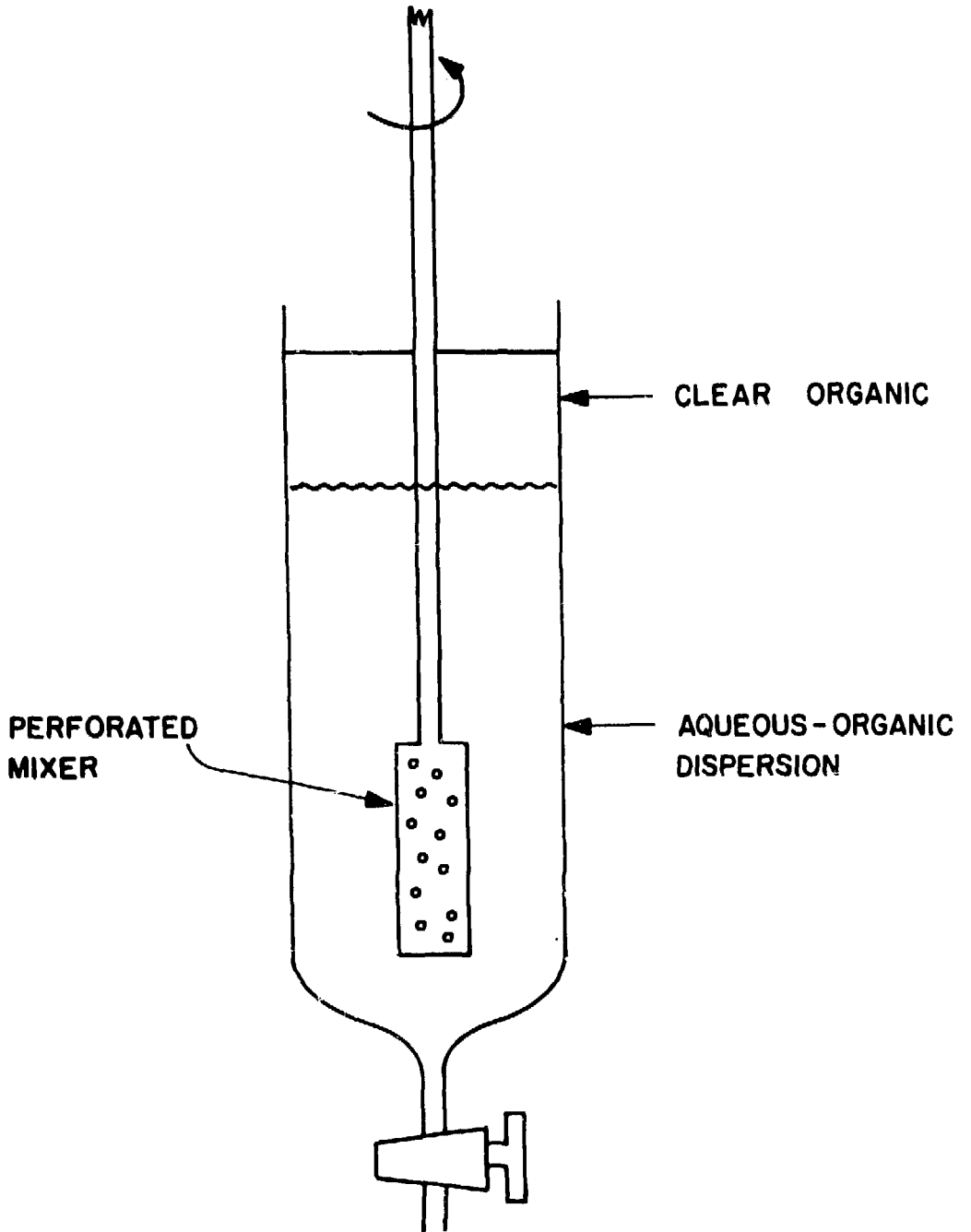
aqueous phase. Analyses were by X-ray fluorescence.

Mathematical calculations

The transfer of the various species are described by the pseudo-first-order rate equations:

$$\frac{dc'}{dt} = - \frac{k'c'a}{v'} + \frac{kca}{v'} \quad \text{(change in aqueous phase concentration)} \tag{1}$$

$$\frac{dc}{dt} = - \frac{kca}{v} + \frac{k'c'a}{v} \quad \text{(change in organic phase concentration)}. \tag{2}$$

At equilibrium,

$$\frac{k'}{k} = D = \frac{c}{c'} \tag{3}$$

In these equations c is the molar concentration of the species, a is the interfacial area, v is the phase volume, k is a rate constant, D is the distribution coefficient, and t is time; the primed symbols refer to the aqueous phase and the unprimed symbols refer to the organic phase.

The rate constants for extraction of uranium (3.4 or 2 $\underline{M}$ HNO$_3$, 1.09 $\underline{M}$ TBP) and thorium (2.0 $\underline{M}$ HNO$_3$, 1.09 $\underline{M}$ TBP) are 7.2 x 10^{-3} cm/sec and 2.1 x 10^{-3} cm/sec, respectively.[1,2]

Zirconium has a number of species in aqueous solutions. The treatment used to prepare the solution for this study is thought to remove oxo-polymers which are inextractable and are not in equilibrium with the extractable species. This treatment then leaves two extractable species, Zr^{4+} and $ZrOH^{3+}$ and an inextractable polymeric species, $Zr_3(OH)_4^{8+}$ which is in equilibrium with the two monomers in the aqueous phase.[3] The rate constant for extraction of Zr^{4+} (3.4 $\underline{M}$ HNO$_3$, 1.09 $\underline{M}$ TBP) is about 3.9 x 10^{-4} cm/sec.[3] The rate constant for extraction of $ZrOH^{3+}$ from 3.4 $\underline{M}$ nitrate

solution by a 1 $\underline{M}$ free (uncomplexed with metal ions or HNO_3) TBP solution is about 5.3×10^{-3} cm/sec.[3] The free TBP concentration of 1.09 $\underline{M}$ TBP in contact with 3.3 $\underline{M}$ HNO_3 containing 0.096 $\underline{M}$ Zr and 0.04 $\underline{M}$ U is estimated to be about 0.39 $\underline{M}$.[4] Since the variation of the rate constant for extraction of $ZrOH^{3+}$ with changes in free TBP concentration is unknown we will assume that the rate constant increases as either the first or second power of the free TBP concentration and compare the calculated results with those obtained experimentally. The two cases to be examined would then have rate constants for extraction of $ZrOH^{3+}$ of about 2.1×10^{-3} cm/sec and 8.1×10^{-4} cm/sec, respectively.

Experimental studies[1,2] have confirmed that the ratio (forward/ reverse) of the rate constants is equal to the distribution coefficient (Eq. 3). Therefore, the reverse rate constants were determined by dividing k' by D. The values of D and k' for 1.09 $\underline{M}$ total TBP and the initial aqueous concentrations are summarized in Table 1. In the calculations the free TBP available for extracting the ions was corrected for the amount of metal ion complex in the organic solution by subtracting twice the metal complex concentration from the TBP concentration. The various forward rate constants and distribution coefficients were then corrected by the TBP power effects given in Table 1. For example, in the uranium-zirconium test the final concentration of TBP not complexed with either uranium or zirconium is about 1.01 $\underline{M}$. Then the uranium distribution would be

$$(\frac{1.01}{1.09})^{1.375}(31) = 27.9.$$

Table 1. Quantities used in transfer calculations

Species	D(1.09 M TBP)	TBP effect (power)	C'_o	k'(cm/sec)	TBP effect (power)
UO_2^{2+} (2 M HNO_3)	19	1.375[1]	0.0042	7.2×10^{-3}	0.5[1]
Th^{4+}	1.26	2.1[2]	0.043	2.1×10^{-3}	1.4[2]
UO_2^{2+} (3.4 M HNO_3)	31	1.375[1]	0.04067	7.2×10^{-3}	0.5[1]
Zr^{4+}	0.149	2[a]	0.022	3.9×10^{-4}	2[3]
$ZrOH^{3+}$	2.64	2[a]	0.0016	8.1×10^{-4}	1[b], 2[b]
$Zr_3(OH)_4^{8+}$	-	-	0.024	-	-

[a]Assumed; overall effect on zirconium distribution is second power.[5]

[b]Assumed; see text.

In all cases the corrections were relatively small. Differential Eq. (2) was solved by a numerical approximation method for the two cases under study. In the calculations, the phase volumes were held constant; this is a reasonable approximation of the experimental system since only a small fraction of the organic phase was removed. In the case of zirconium the quantity extracted is small and the concentration in the aqueous phase was assumed to remain constant (initial condition). The transfers of the two extractable zirconium species ($ZrOH^{3+}$ and Zr^{4+}) were calculated separately and then the individual amounts extracted were added to calculate an overall distribution coefficient for zirconium.

RESULTS

Table 2 gives the experimental organic concentrations for the two experimental tests and aqueous concentrations calculated by material balance. During the runs the amount of the organic phase dispersed with the aqueous phase increased continuously with the time of mixing; thus a data analysis method which is independent of interfacial area was needed. We have chosen to plot the fraction of the equilibrium distribution for one element versus the other. In this form of plot, points on a line of slope 1 (a 45" angle line) have the same separation factor as is obtained at equilibrium. These fractions of equilibrium are also given in Table 2. The solid lines are the calculations from the rate constants.[1-3] The agreement between the calculated and experimental results for U-Th is excellent. In the U-Zr case, agreement is good if it is assumed that the rate constant for extraction of $ZrOH^{3+}$ increases as the first power of the TBP concentration. The agreement of calculation with experiment in these two tests demonstrates

Table 2. Experimental results

t (sec)	Organic concentrations		Calculated aqueous concentrations		D_U/D^*_{UE}	D_{Th}/D^*_{ThE}
	UO_2^{2+} (g/l)	Th^{4+} (g/l)	UO_2^{2+} (g/l)	Th^{4+} (g/l)		
15	0.0175	0.804	0.7665	9.011	0.0013	0.077
30	0.447	1.806	0.373	9.092	0.068	0.172
45	0.64	3.305	0.212	6.843	0.172	0.418
	$D^*_{UE} = 17.6$			$D^*_{ThE} = 1.15$		

t (sec)	UO_2^{2+} (g/l)	Zr (g/l)	UO_2^{2+} (g/l)	Zr (g/l)	D_U/D^*_{UE}	D_{Zr}/D^*_{ZrE}
15	2.268	0.031	7.41	7.64	0.012	0.066
35	7.566	0.125	2.55	7.56	0.106	0.269
60	9.935	0.214	0.597	7.49	0.596	0.465
	$D^*_{UE} = 27.9$			$D^*_{ZrE} = 0.0614$		

*Equilibrium distributions.

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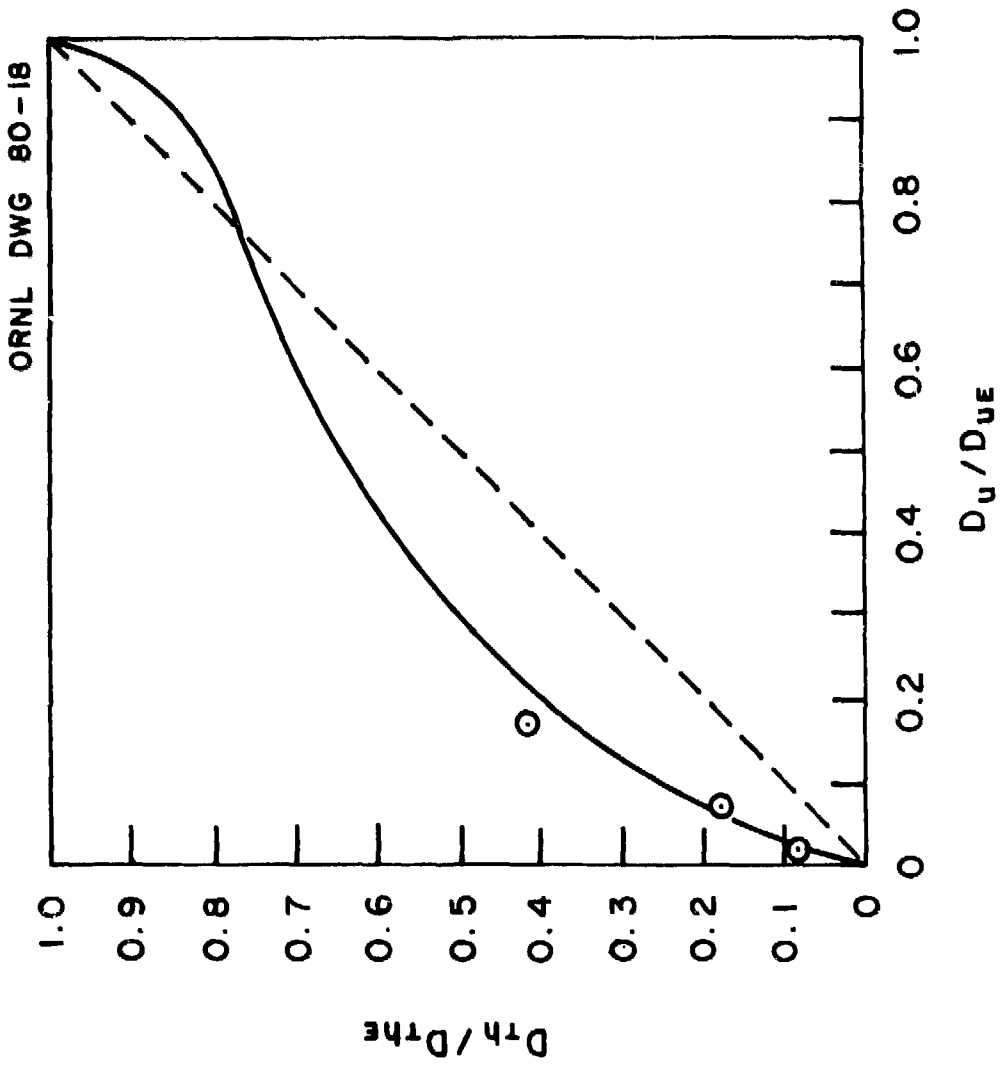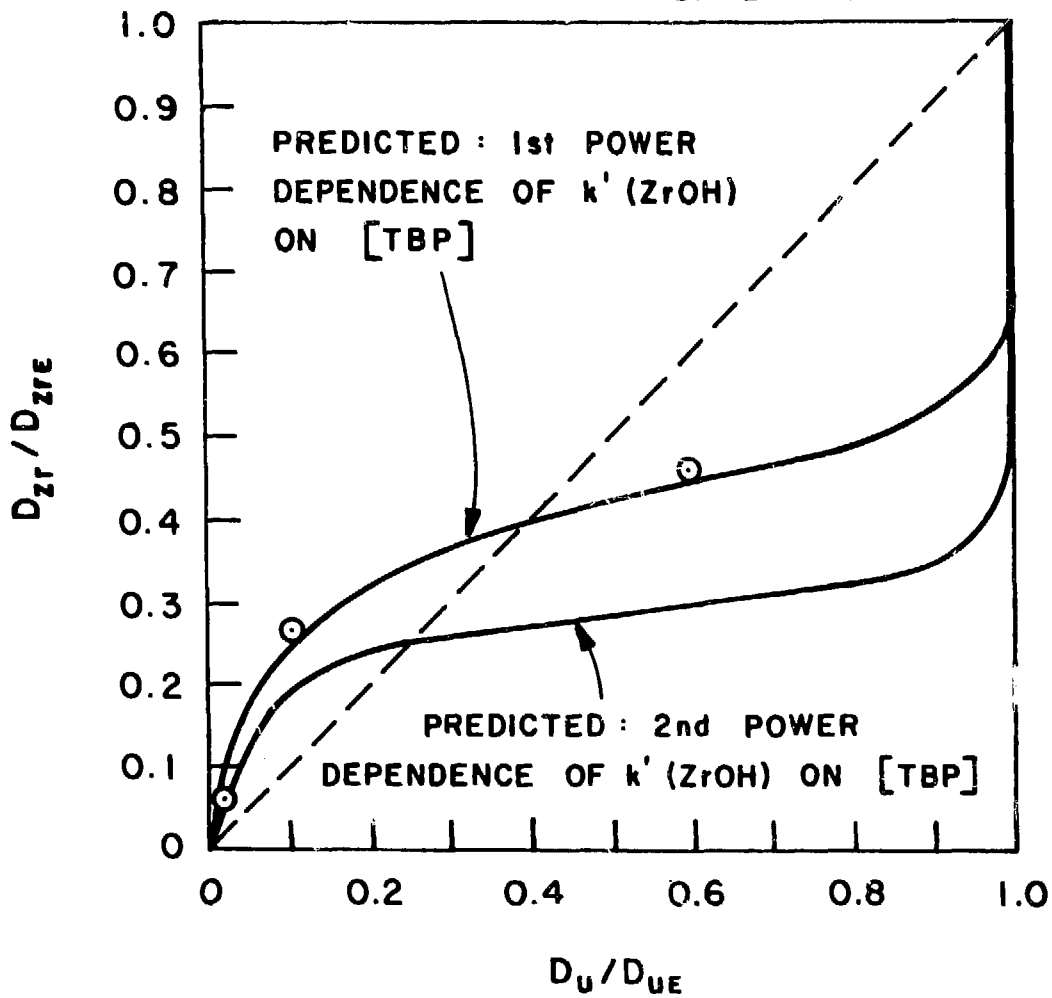
the usefulness of the rate constant data for predicting the behavior of
extraction under non-equilibrium conditions. In the case for Th-U
the separation factor defined as D_U/D_{Th} is seen to be lower than the
equilibrium separation factor over much of the non-equilibrium region.
The tiny advantage between 0.8 and 1.0 on the abscissa is insignificant.
However, in the case of U-Zr, much larger separation factors (D_U/D_{Zr}) are
to be obtained by operating slightly below the uranium equilibrium.
The unusual shape of the data for this system is a result of the behavior
of the $ZrOH^{3+}$ ion which is quite slow in its approach to equilibrium.
The calculated transfer of Zr^{4+}, $ZrOH^{3+}$, and total zirconium to the
organic phase is shown in Fig. 4. The slow transfer of $ZrOH^{3+}$ definitely
gives a significant advantage to operation short of the zirconium
equilibrium.

CONCLUSIONS

1. The calculated and experimental transfer behavior are in good
   agreement demonstrating the utility of the measured transfer rate
   constants.

2. The single-stage separation factor for U-Th is lower for short contact
   times than for equilibrium conditions.

3. The single-stage separation factor for U-Zr can be significantly
   improved by non-equilibrium operation.
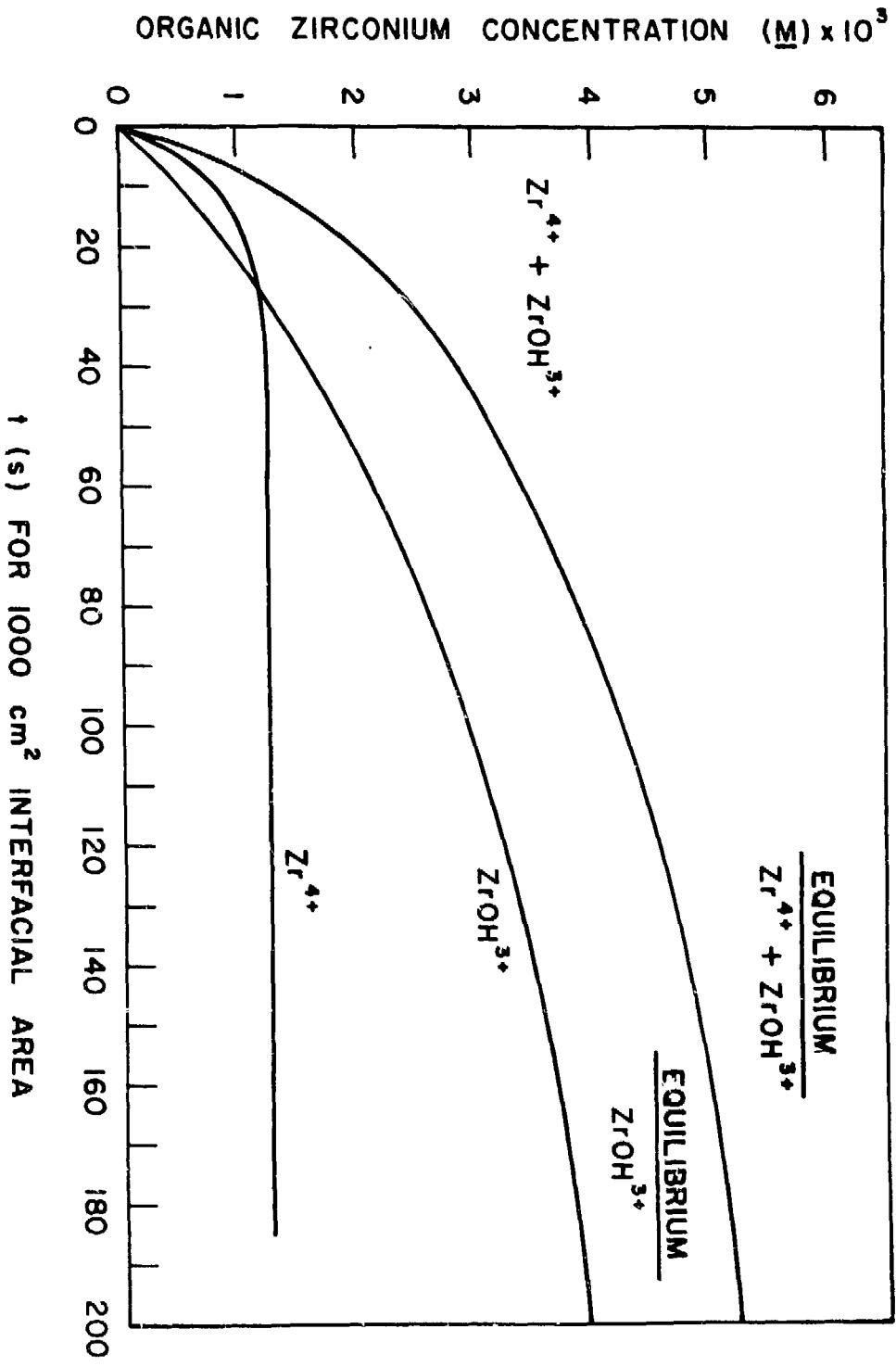
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ACKNOWLEDGMENTS

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