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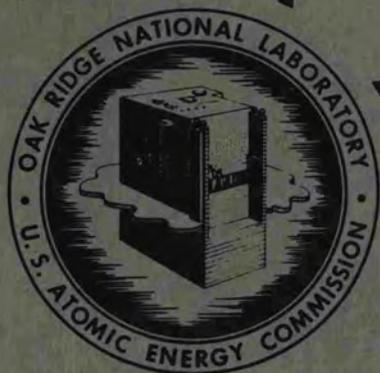
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CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT OF  
PROCESS TEST SECTION  
FOR JULY, 1956

A. D. Ryon and K. O. Johnson

Date Issued

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ABSTRACT

Batch kinetic studies were made of the stripping step using sodium carbonate in a Dapex process for the recovery of uranium from leach liquors. The data are treated in the manner of Hixon and Smith to yield a reaction rate constant which is directly proportional to holdup time. It was found that the rate constant for this system is inversely proportional to the sodium carbonate excess in the stripping solution and to the power input to the mixing vessel.

NOTICE

The data presented in this report are preliminary, and are published in a formal report only to permit rapid dissemination of information to interested persons.

## BATCH KINETIC STUDIES

J. R. Buchanan

### STRIPPING

#### Introduction

Stripping kinetics of a Dapex-type organic using sodium carbonate as the stripping agent have been studied. The experiments were made in order to find the order of magnitude of the stripping rate constants for an extract of fairly high uranium loading. In addition the mixing power and excess carbonate were varied independently to show their relative effects on the rate constants.

Apparatus and Procedure. The reactor illustrated in Fig. 1 consisted of a 6" ID glass pipe fitted with four equally spaced 1/2" baffles. A 3" diameter, 4-bladed turbine of the standard proportions<sup>1</sup> was used.

Making a run consisted of introducing the loaded organic, (0.16M Di2EHPA in kerosene with 3.5% TBP) to the cell, setting the desired mixer speed, adding the stripping agent and taking the gradient samples at the proper time interval. Gradient samples were dipped from the reactor so that they were instantaneous. Primary break times in the order of 10-40 seconds were noted. A haze persisted in the organic phase so that the samples were centrifuged as quickly as possible to give clear solutions.

#### Treatment of Data

The kinetic information obtained is treated in the manner of Hixon and Smith<sup>2,4</sup>. This method yields a reaction rate constant, K, that is directly proportional to holdup time. Therefore, low K values are to be desired.

- 
1. J. H. Rushton, Chem. Engr. Prog., 50, 587-589 (1954).
  2. A. W. Hixon and M. I. Smith, Ind. Eng. Chem., 41, 973 (1948).
  3. R. B. McMullin and M. Weber, Trans. Amer. Inst. Chem. Engrs., 31, 409 (1935).
  4. R. E. Treybal, Liquid Extraction, 263, New York, McGraw-Hill Book Co. (1951).

DIMENSION RATIOS OF TURBINE  
 $D:D_p:L_b:W = 20:15:5:4$

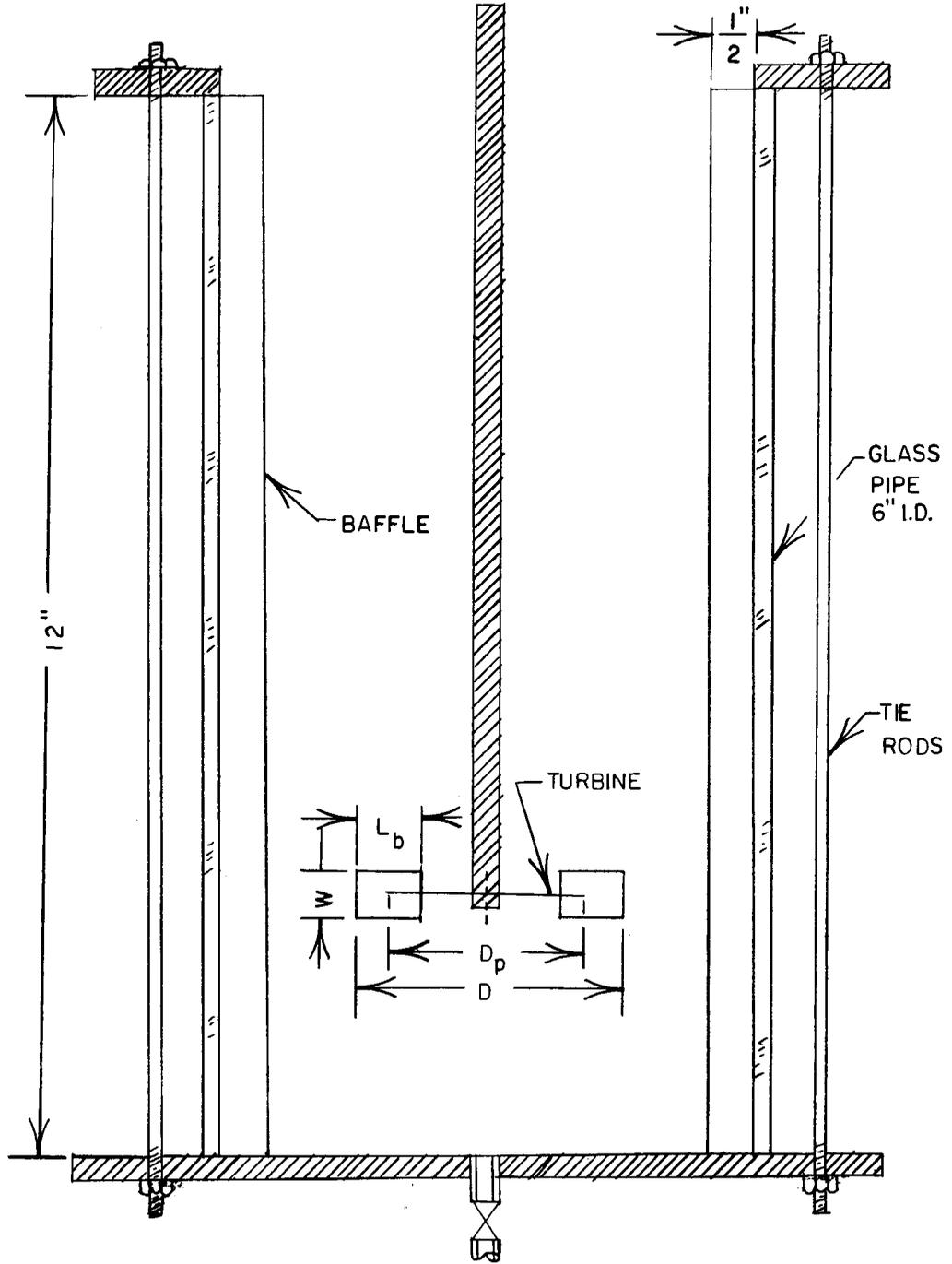


FIGURE 1— DETAILS OF BATCH MIXER

K is defined as:

$$K = - \frac{\theta}{\ln(1-E)} \quad \text{--- (1)}$$

where  $\theta$  is the time in seconds and E is the batch stripping efficiency. In turn E is defined as:

$$E = \frac{C_0 - C_t}{C_0 - C_{eq}} \quad \text{--- (2)}$$

where  $C_0$  is the initial concentration of the reactant being measured,  $C_{eq}$  the equilibrium concentration, and  $C_t$  the concentration at time  $\theta$ .

The residence time,  $\theta_H$ , required in a continuous mixer can be predicted from K by use of the equation<sup>3,4</sup>:

$$\theta_H = \frac{KE_{av}}{1-E_{av}} \quad \text{--- (3)}$$

where  $E_{av}$  is the desired stage efficiency in a continuous reactor.

In order to illustrate the procedure for the evaluation of K, the data for run 11 are analyzed in detail. (Run 11 was chosen since more reaction data was available before equilibrium was reached.) The rate data obtained were:

Mixing Time (sec)	Uranium in Organic Phase (g/l)
0	5.2
10	2.9
20	1.5
30	.68
60	.37
120	.37
240	.38
480	.36

The equilibrium concentration was assumed to be the average of the last four analyses; therefore:

$$\begin{aligned} C_0 &= 5.2 \text{ g/l} \\ C_{eq} &= .37 \text{ g/l} \\ C_0 - C_{eq} &= 4.8 \text{ g/l} \end{aligned}$$

The 1-E values were calculated as follows:

	Time (sec)		
	<u>10</u>	<u>20</u>	<u>30</u>
$C_t$	2.9	1.5	0.68
$C_t - C_{eq}$	2.5	1.1	.31
$1 - E = \frac{C_t - C_{eq}}{C_0 - C_{eq}}$	0.5	.23	.064

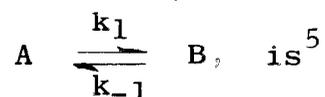
In Fig. 2, 1-E was plotted versus time. A straight line was drawn through the ordinate value of  $\ln 1$  and the plotted points to give a conservative K value. The value for  $\Theta$ , 32.4, at 1-E = 0.1 was read from the plot.

Then

$$K = \frac{\Theta}{-\ln(1-E)} = \frac{32.4}{-\ln(0.1)} = \frac{32.4}{2.3} = 14.1$$

The method just illustrated was derived on the basis of a diffusion controlled reaction and is, therefore, limited to first order reactions. It is not known whether the stripping step is diffusion or chemical controlled but as shown in the illustration the data correlated sufficiently well to give a useful reaction constant.

It is of interest to see the relation of the reaction constant, K, to the reaction constant for a first order equilibrium reaction. The general equation for the first order equilibrium reaction,



$$k_1 + k_{-1} = \frac{1}{t} \ln \frac{x_e}{x_e - x} \quad \text{---} \quad (5)$$

where  $k_1$  and  $k_{-1}$  are the specific rates in forward and reverse direction,  $t$  the time of reaction,  $x$  is the concentration of B and  $x_e$  the concentration of B at equilibrium.

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5. K. J. Laidler, Chemical Kinetics, 18, New York, McGraw-Hill (1950).

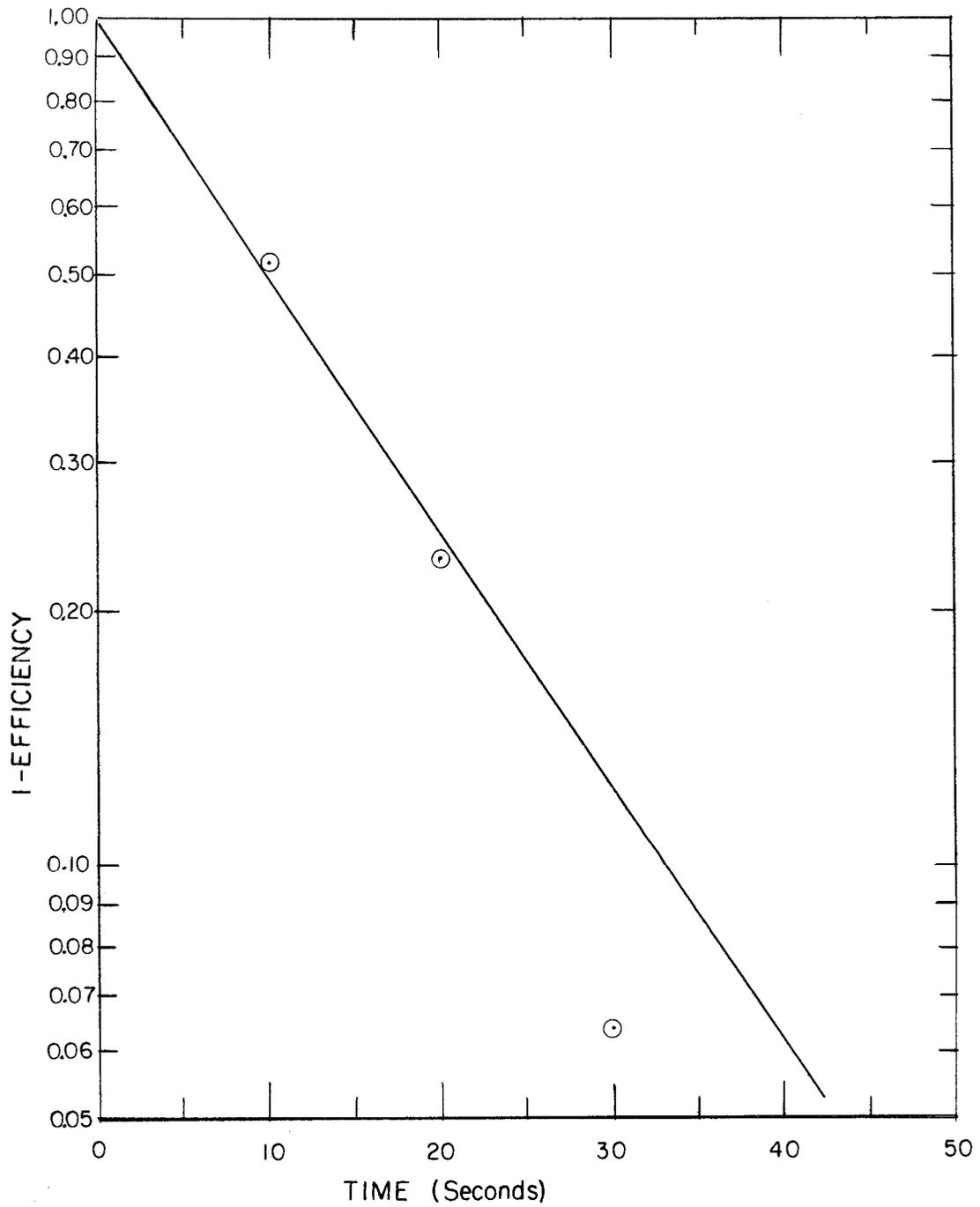


FIGURE 2 - STRIPPING EFFICIENCY

For similar nomenclature, if we let  $C_0$  be the initial concentration of the uranium in the organic phase as represented by A, and  $C_t$  and  $C_{eq}$  represent the uranium concentration in the organic at reaction time  $t$  and equilibrium, respectively, it follows that

$$C_0 - C_t = x \text{ - - - - -} \quad (6)$$

and  $C_0 - C_{eq} = x_e \text{ - - - - -} \quad (7)$

Substitution into equation (5) yields:

$$k_1 + k_{-1} = \frac{1}{t} \ln \frac{C_0 - C_{eq}}{C_t - C_{eq}} \text{ - - - - -} \quad (8)$$

Let  $K^1$ , the sum of  $k_1 + k_{-1}$ , be the effective reaction constant.

$$\therefore K^1 = \frac{1}{t} \ln \frac{C_0 - C_{eq}}{C_t - C_{eq}} \text{ - - - - -} \quad (9)$$

Taking equation (1) and substituting equation (2) yields:

$$K = - \frac{\theta}{\ln \left( \frac{C_t - C_{eq}}{C_0 - C_{eq}} \right)}$$

which can be transposed to

$$K = \frac{\theta}{\ln \left( \frac{C_0 - C_{eq}}{C_t - C_{eq}} \right)}$$

Since  $\theta$  and  $t$  are equal by definition

$$K = \frac{1}{K^1}$$

the units of  $K$  are seconds while  $K^1$  is reported in reciprocal seconds.

## RESULTS AND DISCUSSION

### Effect of Reagent Excess

As is shown in Table 1, K is inversely proportional to the amount of carbonate excess. As the carbonate excess increases from 19 to 55 percent excess there is a decrease in the value of K from 14.1 to 5.4 sec. This relationship is shown graphically in Fig. 3.

The primary phase break in all stripping runs was fast, in the order of 10 to 40 seconds. After five minutes of settling there was still a residual entrainment of aqueous in the organic phase as is shown in Table 1. However, this was easily removed by centrifugation or filtration. There was no residual organic entrained in the aqueous phase.

### Effect of Power Input

Power input, as would be expected, showed an inverse effect on the value of K as can be seen in Table 2. At a power level of 0.063 hp/gal the reaction reached equilibrium so quickly that there were no points for determining the actual value of K but it must be less than 2.1 seconds, the value of the next lower power level.

The aqueous entrainment in the organic phase increased from 0.20 to 0.53 volume percent for an increase in the power from 0.006 to 0.019 hp/gal. An additional increase in the power made no difference in the entrainment indicating a leveling off with the power input. Again there was no organic entrained in the aqueous phase.

### Effect of Two Passes

The data on stripping in which the organic from the first pass is later contacted with fresh carbonate solution is presented in Table 3. The rate on the second pass was too fast to yield any points for determination of K.

The entrainment of aqueous in the organic phase was slightly higher on the second than on the first pass. There was no entrainment in the aqueous phase.

### Future Work

No additional work is planned on batch stripping kinetics. A group of runs will be made on the Dapex extraction of a high uranium-vanadium liquor.

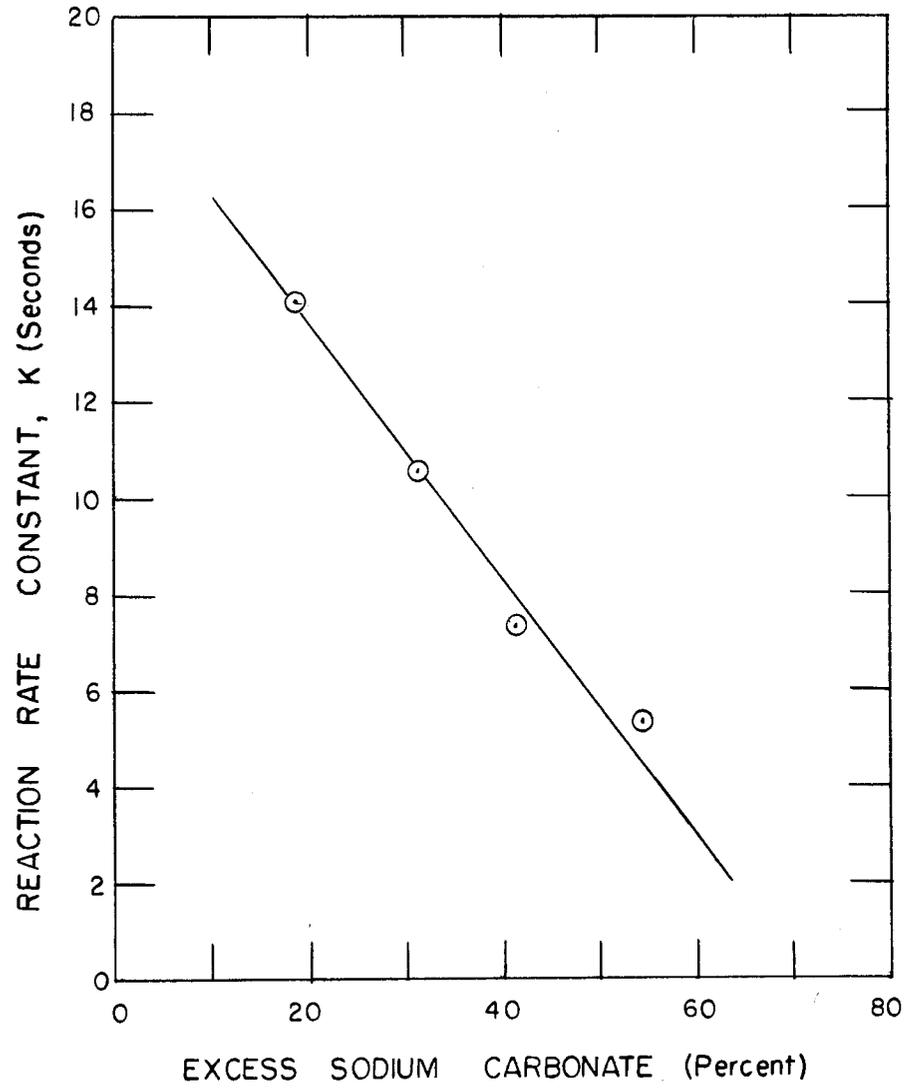


FIGURE 3 — EFFECT OF CARBONATE EXCESS  
ON REACTION RATE CONSTANT

TABLE 1. EFFECT OF CARBONATE EXCESS ON STRIPPING RATE

Three-inch turbine at 420 rpm  
 D/T ratio\*: 0.5  
 Power input: 0.006 hp/gal  
 Phase ratio: 5 org/l aq  
 Organic: 0.16M Di2EHPA in kerosene with 3.5 g TBP/l

Run No.	Na <sub>2</sub> CO <sub>3</sub> Excess (%)	Na <sub>2</sub> CO <sub>3</sub> Conc. (molarity)	K (sec)	Uranium Concentration in Organic (g/l)								Entrainment in Organic** (vol %)
				Mixing Time (sec)								
				0	10	20	30	60	120	240	480	
1	55	0.95	5.4	5.2	1.07	0.32	0.29	0.30	0.31	0.31	0.31	0.20
7	41	.87	7.4	5.2	1.58	.33	.30	.33	.32	.32	.32	.40
9	32	.81	10.6	5.2	2.3	.56	.31	.36	.33	.33	.33	.33
11	19	.73	14.1	5.2	2.9	1.5	.68	.37	.37	.38	.36	.33

\*Diameter of turbine/tank diameter.

\*\*After 5 minutes' settling.

TABLE 2. EFFECT OF POWER INPUT ON STRIPPING RATE

Stripping agent: 0.95M Na<sub>2</sub>CO<sub>3</sub>  
 Carbonate excess: 55%  
 Three-inch turbine  
 D/T ratio\*: 0.5  
 Phase ratio: 5 org/1 aq  
 Organic: 0.16M Di2EHPA in kerosene with 3.5 g TBP/l

Run No.	Power (hp/gal)	Turbine Speed (rpm)	K (sec)	Uranium Concentration in Organic (g/l)								Entrainment Aqueous in Organic** (vol %)
				Mixing Time (sec)								
				0	10	20	30	60	120	240	480	
1	0.006	420	5.4	5.2	1.1	0.32	0.29	0.30	0.31	0.31	0.31	0.20
3	.019	630	2.1	5.2	.34	.30	.31	.30	.30	.30	.30	.53
5	.063	945	<2.1	5.2	.31	.29	.28	.30	.29	.30	.30	.53

\*Diameter of turbine/tank diameter.

\*\*After 5 minutes' settling.

TABLE 3. EFFECT OF TWO PASSES ON STRIPPING RATE

Stripping agent: 0.95M Na<sub>2</sub>CO<sub>3</sub>  
 Three-inch turbine at 630 rpm  
 D/T ratio\*: 0.5  
 Power input: 0.019 hp/gal  
 Phase ratio: 5 org/l aq  
 Organic: 0.16M Di2EHPA in kerosene with 3.5 g TBP/l

Run No.	Pass	Na <sub>2</sub> CO <sub>3</sub> Excess (%)	K (sec)	Uranium Concentration in Organic (g/l)								Entrainment Aqueous in Organic** (vol %)
				Mixing Time (sec)								
				0	10	20	30	60	120	240	480	
3	1st	55	2.1	5.2	0.34	0.30	0.31	0.30	0.30	0.30	0.30	0.53
3A	2nd	>500	<2.1	.30	.017	.018	.019	.018	.016	.018	.018	.73

\*Diameter of turbine/tank diameter.

\*\*After 5 minutes' settling.