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DEUTERATION AND DEDEUTERATION OF PROTOTYPE NPD-2 RESIN COLUMNS

by

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DISCLAIMER

SUMMARY

A study of the deuteration of NPD-2 resin columns and dedeuteration by light water displacement is reported and optimum displacing velocities are determined. Comparison with data of other workers is used to point out desirable design features.

A method of calculating longitudinal dispersion coefficients from effluent concentration profiles is presented and agreement established with the results of workers with other systems and column arrangements.

A method is outlined for estimating effluent concentration profiles from bed packing characteristics and column dimensions.

INTRODUCTION

In heavy water moderated reactors both radiation decomposition of the water and corrosion of materials of construction are reduced by controlling the purity of the water. In the NPD reactor it is planned to do this by using mixed-bed ion exchange resin purification systems in the primary coolant and moderator circuits.

Before the resin is introduced into the heavy water circuits it must be "deuterated" by replacing the H^+ and OH^- ions at the exchange sites by D^+ and OD^- ions. Deuteration by a slow upward flow of D_2O through a resin bed containing H_2O has been successfully carried out for a number of years but no study to determine the optimum flow rate has been reported.

In the NPD system it is planned to discard the resin container as well as the resin itself when the latter becomes exhausted. Before the resin can be discarded it will be necessary for economic reasons to recover the associated heavy water. At present it is planned to do this by draining followed by drying with inert gas from which the D_2O can be recovered. This system is used in the NRU reactor.

It has been demonstrated (1) that 'dedeuteration' can be accomplished by displacing the heavy water with a slow downward flow of light water. Such a method of dedeuteration of resin columns might be preferable to inert gas drying. The purpose of the study reported here was to establish optimum conditions for the deuteration of the NPD resin columns and dedeuteration by light water displacement. The data on dedeuteration can be used to compare light water displacement with inert gas drying.

THEORY

The optimum flow rate will be such that a sharp interface between the light and heavy water is maintained during the operation in order that the amount of heavy water downgraded with light water is kept to a minimum. If the flow rate through the column is too high mechanical mixing of the water will occur. If it is too low molecular diffusion will become important.

In recent years the longitudinal mixing of fluids in pipe lines and packed beds has received increasing attention. Dankwerts (2) suggested an analysis based on a mathematical model assuming no radial concentration gradients and a flat velocity profile. In this treatment the mixing occurring in the void spaces of a packed column is characterized by a longitudinal dispersion coefficient analogus to the molecular diffusion coefficient used in the treatment of non-flowing systems.

Levenspiel and Smith (3) refined this treatment to show that:

$$C = \frac{1}{\sqrt{2\pi\left(\frac{v\theta}{V}\right)\left(\frac{De}{UL}\right)}}\; e^{-\frac{1-\frac{v\theta}{V}}{4\left(\frac{VO}{V}\right)\left(\frac{De}{UL}\right)}} \qquad (1)$$

$\frac{De}{UL}$ is a measure of the sharpness of the interface and $\frac{v\theta}{V}$ is the number of bed void volumes that have passed through the system. For the condition of no mixing $\frac{De}{UL} = 0$ and $\frac{v\theta}{V} = 1$ the weight fraction of displacing fluid in the effluent will rise abruptly to 0 to 1. In general for small values ($\ll 1$) of $\frac{De}{UL}$, $\frac{V\theta}{V}$, will increase from slightly less than 1 for C = 0 to slightly more than 1 for C = 1. For small values of $\frac{De}{UL}$ and $\frac{v\theta}{V} \simeq 1$ equation 1 reduces to:

$$C = \frac{1}{\sqrt{2\pi\frac{De}{UL}}}\; e^{-\frac{1-\frac{v\theta}{V}}{4\frac{De}{UL}}} \qquad \left(\frac{De}{UL} \ll 1\right)$$

This can be shown to be the equation for a Gaussian distribution the variance of which

$$\sigma^2 = 2\frac{De}{UL}$$

A plot of concentration of displacing fluid on the probability scale against total weight (or volume) of fluid fed on the linear scale of normal probability paper should give a straight line. From the plot 2σ equals the volume of feed required to increase the outlet concentration from 16% to 84%. The void volume of the bed is the volume at which the outlet concentration is 50%. Before $\frac{De}{UL}$ can be calculated the value of σ obtained from the plot must be expressed as a fraction of the void volume.

A further consequence of equation (1) is that for given values of D and U, $\sigma \propto \frac{1}{\sqrt{L}}$

An alternative treatment due to Aris and Amundson (6) considers a packed bed to be a series of cells in each of which perfect mixing occurs. This treatment leads to the result that the concentration of displacing fluid in the effluent should follow the Posson distribution Law. As the number of cells

in series becomes large (100) the Posson distribution approaches the Gaussian distribution closely. Since the number of cells is equal to the bed length divided by the mean particle diameter, the number of cells is very large in a two foot bed of 100 mesh resin. This treatment leads to the same result as the treatment of Levenspiel and Smith(3).

Several authors have presented correlations relating the longitudinal dispersion coefficient to the size of bed particles and interstitial velocity. Of these the equation

$$D = 2.92\, d_p \left(\frac{U}{e}\right)^{1.08}$$

due to Ebach and White (4) appears to be the most readily usable.

It will be shown from the results of this study that longitudinal dispersion coefficients determined by the method of Levenspiel and Smith agree with those calculated from the Ebach and White correlation at low displacing velocities.

PREVIOUS WORK

Hart et al (7) and Frisch and Kunin (9) have reported on deuteration of resins in small (4" i.d.) experimental columns. Chenouard (8) gives results on routine deuteration of larger columns (40" i.d.).

Bertsche (1) reports on two dedeuteration runs in a large (48" i.d.) column.

The results of this study will be compared with those of the above authors with a view to indicating design features desirable in resin columns to be deuterated and dedeuterated by the displacement method.

EQUIPMENT

A schematic diagram of the equipment is shown in Figure 1.

The feed pump used was a dual head diaphragm type positive displacement pump made by the Milton Roy Company. The valves used were three way solenoid valves.

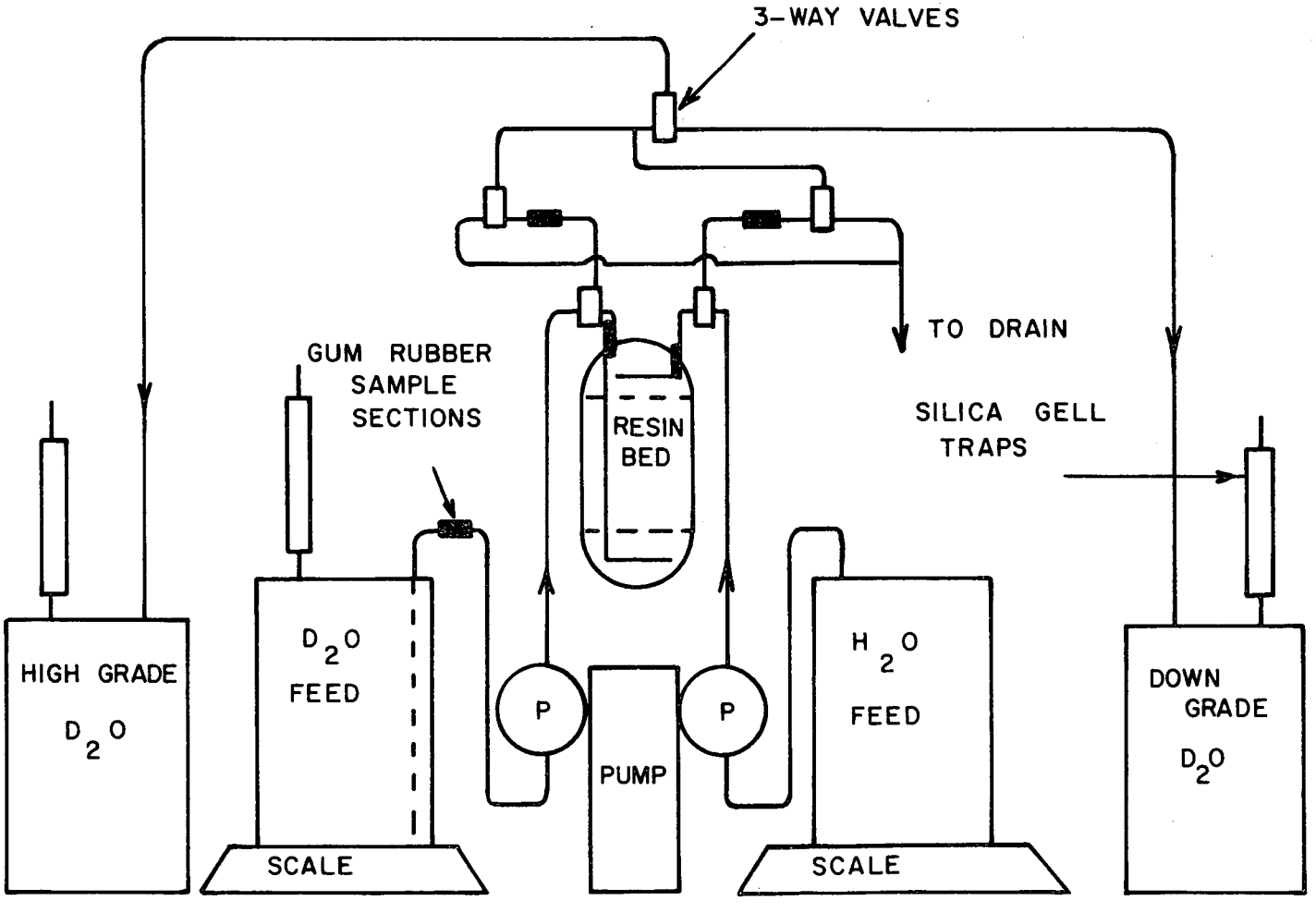
The NPD resin column tested is shown in sections in Figure 1A. The column was designed to eliminate as far as possible stagnant pockets in which fluid could settle.

The distributors were shaped to fit the column ends. The resin bed was supported between distributors to reduce the tendency for channelling through the bed to occur.

Dished ends were used to make the transition from fluid velocity in the pipe to velocity in the column more gradual than would occur with an abrupt change in section.

FIGURE I.

SCHEMATIC LAYOUT OF APPARATUS



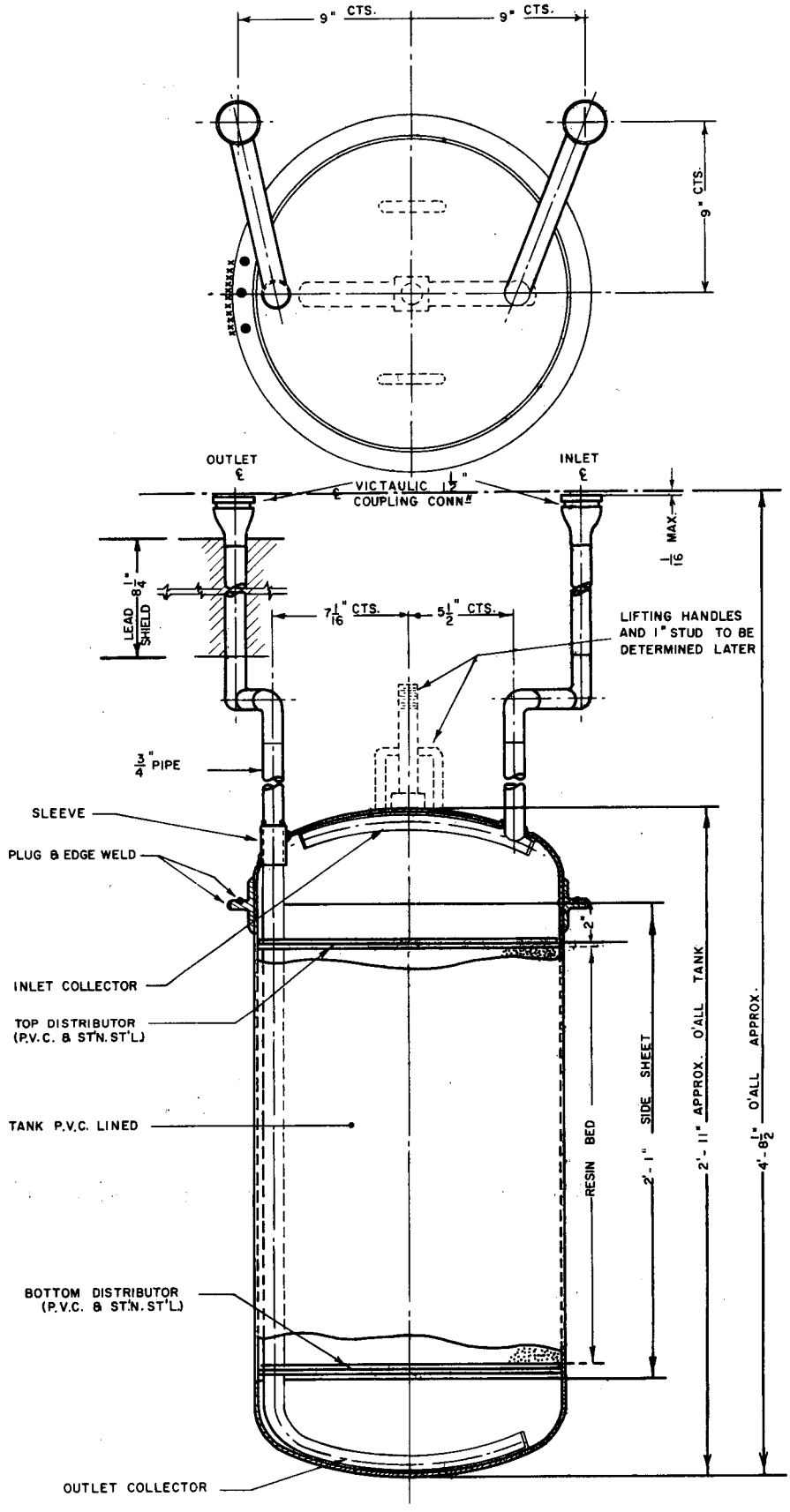


FIG. 1A.

DETAIL OF RESIN COLUMN

OPERATING PROCEDURE

The column was weighed as received, filled with water through the bottom inlet with vacuum applied to the outlet, and weighed again.

The difference in weights was used as a measure of the void volume of the column.

With the column filled with light water and the light water feed line disconnected, heavy water was pumped in at the desired rate through the bottom inlet. Samples of the effluent were taken by syringe through the gum rubber section of the outlet line at 5 lb intervals over the range 160 - 250 lb. Samples were injected immediately into previously dried sample bottles fitted with rubber diaphragm caps.

The deuterated column was allowed to stand overnight and then dedeuterated.

The dedeuteration procedure was was follows. With the heavy water feed line disconnected, light water was fed at the desired rate through the top inlet and the heavy water displaced through the bottom. Samples of the effluent were taken at start up, after 50 lb, and at 5 lb intervals over the range 160 - 250 lb.

During deuteration the first 160 lb of effluent were discharged to the drain. 70 lb were collected in the downgraded D_2O receiver and the remainder in the highgrade receiver.

During dedeuteration the first 180 lb were collected in the highgrade receiver, the next 50 lb in the low grade receiver, and the remainder sent to the drain.

RESULTS

Weight of column + water = 352 lb
Weight of column alone = 165 lb
Weight of water in column = 187 lb

The data obtained are shown as plots of wt % D_2O in the effluent vs total weight of displacing fluid fed in Figures 2 - 6.

From these plots dispersion coefficients were calculated. The amount of D_2O downgraded will be a minimum when $\frac{De}{UL}$ is a minimum. Figure 7 shows a plot of $\frac{D}{U}$ vs. U.

The weights of D_2O downgraded in each run and the costs for each deuteration - dedeuteration cycle are shown in Table 1.

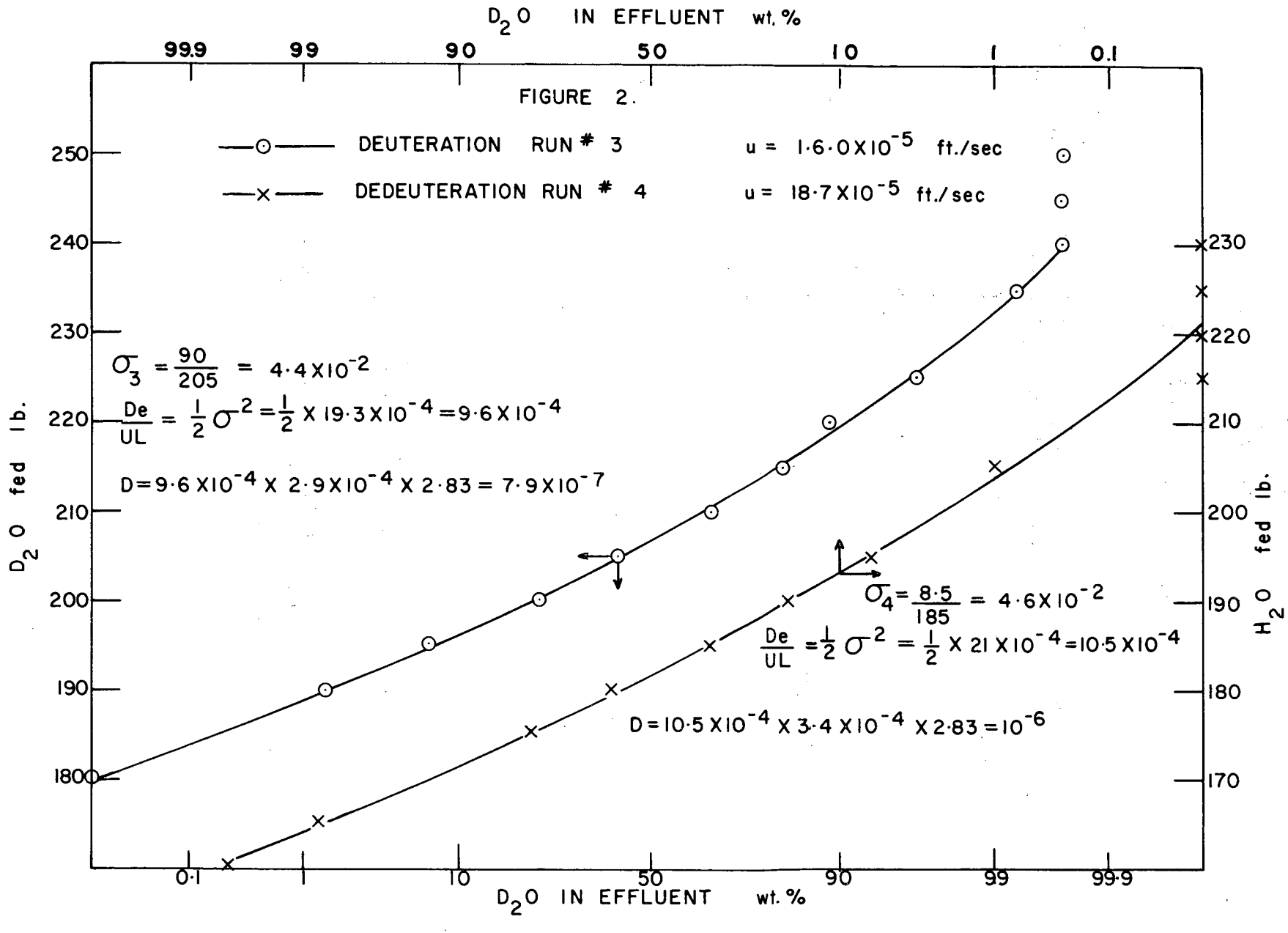
Table 1

Cost of D_2O Re-enrichment

Run No.*	Linear Velocity Through Bed	D_2O in Exchange Band	Cost of** Recovery	Cost per Deuteration - Dedeuteration Cycle
	ft/sec	lb	$	$
4	18.7×10^{-5}	22.2	91	211
3	16.0×10^{-5}	32.5	120	
12	14.9×10^{-5}	19.1	79	189
11	14.3×10^{-5}	29.8	110	
8	9.9×10^{-5}	12.6	53	153
7	9.3×10^{-5}	26.7	100	
10	6.6×10^{-5}	19.0	78	178
9	6.0×10^{-5}	26.2	100	
5	3.9×10^{-5}	28.9	101	171
6	3.7×10^{-5}	16.7	70	

* Odd numbered runs are deuteration runs
Even numbered runs are dedeuteration runs

** The costs of recovery were obtained from the average D_2O concentration in the exchange band and the cost data given in Figure 11.


D2O IN EFFLUENT wt.%
99.9
99
90
50
10
1
0.1
FIGURE 2.
DEUTERATION RUN # 3
u = 16.0X10-5 ft./sec
DEDEUTERATION RUN # 4
u = 18.7X10-5 ft./sec
σ3 = 90/205 = 4.4X10-2
De/UL = 1/2 σ-2 = 1/2 X 19.3X10-4 = 9.6X10-4
D = 9.6X10-4 X 2.9X10-4 X 2.83 = 7.9X10-7
σ4 = 8.5/185 = 4.6X10-2
De/UL = 1/2 σ-2 = 1/2 X 21X10-4 = 10.5X10-4
D = 10.5X10-4 X 3.4X10-4 X 2.83 = 10-6
D2O fed lb.
H2O fed lb.
250
240
230
220
210
200
190
180
170
0.1
1
10
50
90
99
99.9
D2O IN EFFLUENT wt.%

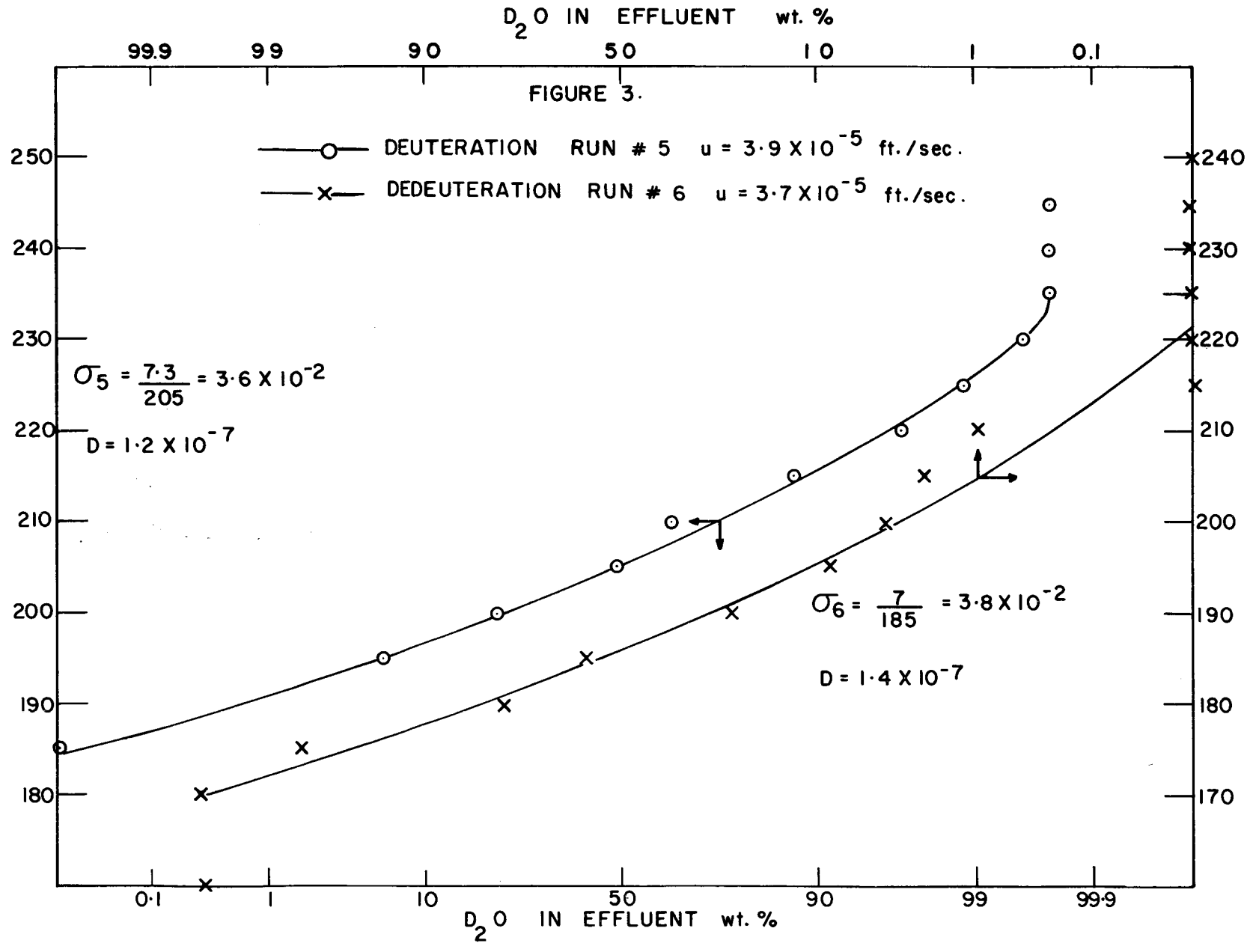
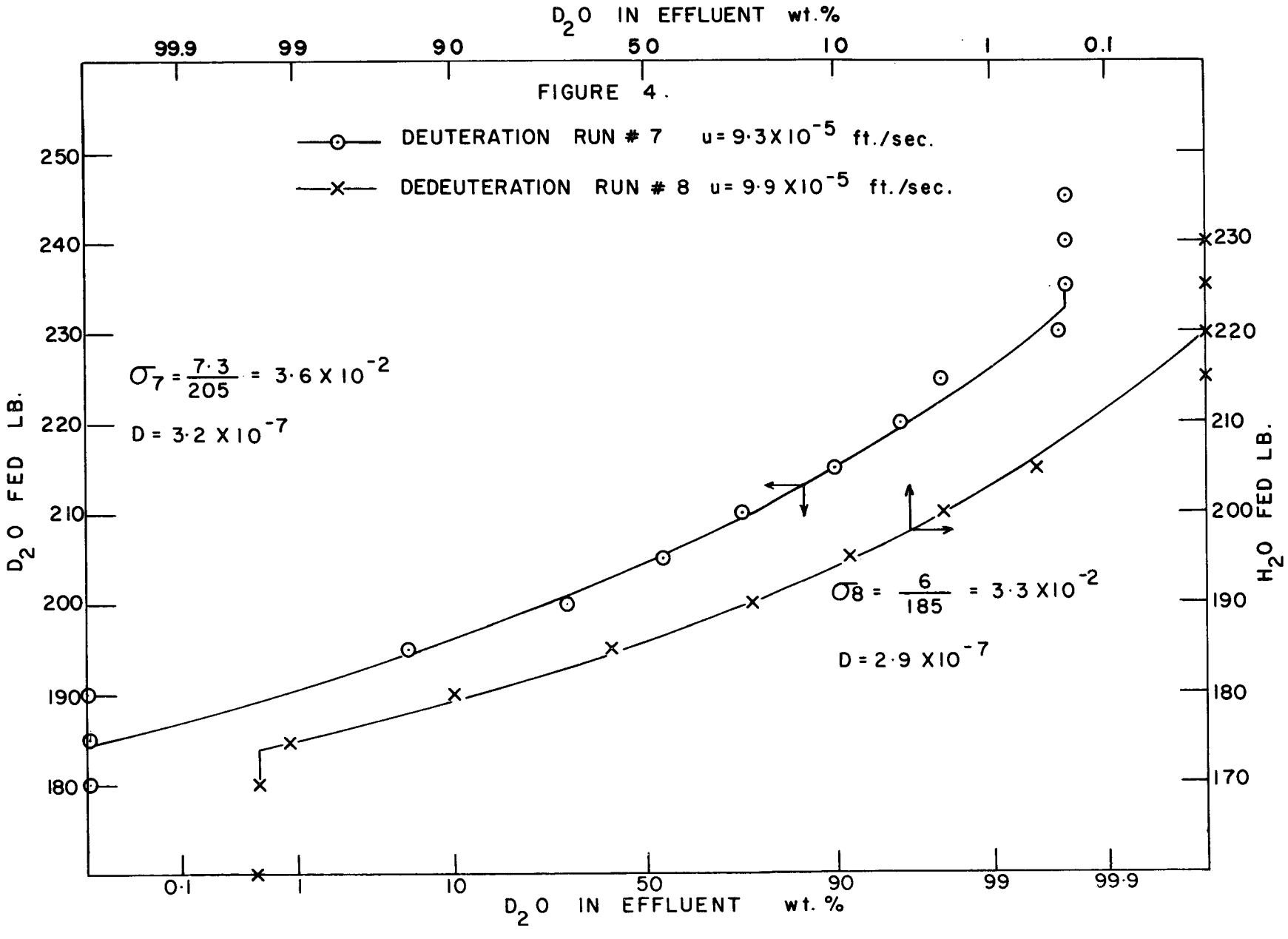
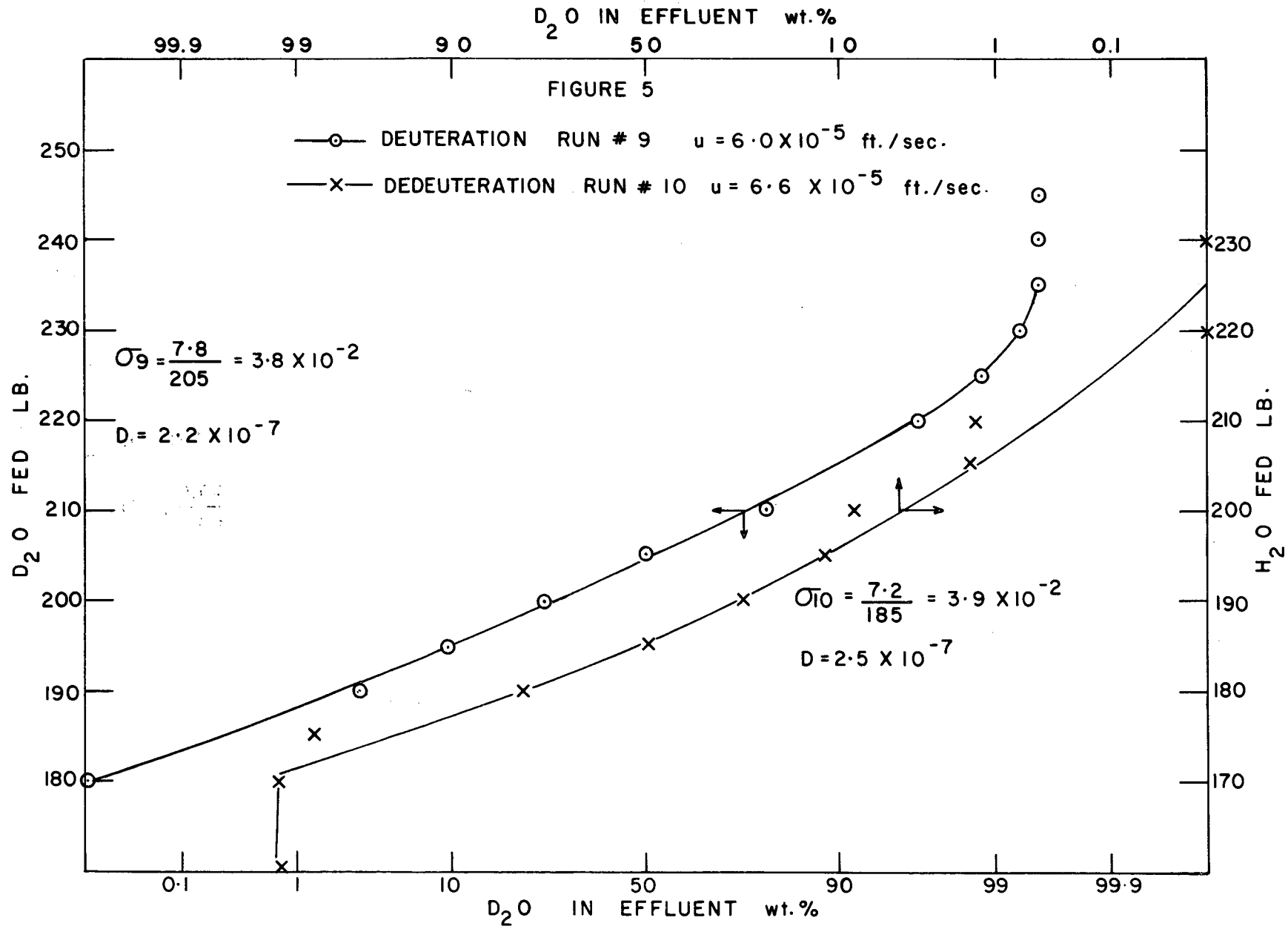

D_2O IN EFFLUENT wt. %
99.9
99
90
50
10
1
0.1
DEUTERATION RUN # 5 $u = 3.9 \times 10^{-5}$ ft./sec.
DEDEUTERATION RUN # 6 $u = 3.7 \times 10^{-5}$ ft./sec.
250
240
230
220
210
200
190
180
240
230
220
210
200
190
180
170
$\sigma_5 = \frac{7.3}{205} = 3.6 \times 10^{-2}$
$D = 1.2 \times 10^{-7}$
$\sigma_6 = \frac{7}{185} = 3.8 \times 10^{-2}$
$D = 1.4 \times 10^{-7}$
0.1
1
10
50
90
99
99.9
D_2O IN EFFLUENT wt. %

FIGURE 3.


D_2O IN EFFLUENT wt.%
99.9
99
90
50
10
1
0.1
FIGURE 4.
DEUTERATION RUN # 7 u = 9·3X10^{-5} ft./sec.
DEDEUTERATION RUN # 8 u = 9·9 X10^{-5} ft./sec.
250
240
230
220
210
200
190
180
D_2O FED LB.
$\sigma_7 = \frac{7·3}{205} = 3·6 X 10^{-2}$
$D = 3·2 X 10^{-7}$
$\sigma_8 = \frac{6}{185} = 3·3 X 10^{-2}$
$D = 2·9 X 10^{-7}$
230
220
210
200
190
180
170
H_2O FED LB.
0·1
1
10
50
90
99
99·9
D_2O IN EFFLUENT wt. %


D_2O IN EFFLUENT wt.%
99.9
99
90
50
10
1
0.1
FIGURE 5
DEUTERATION RUN # 9 $u = 6.0 \times 10^{-5}$ ft./sec.
DEDEUTERATION RUN # 10 $u = 6.6 \times 10^{-5}$ ft./sec.
$\sigma_9 = \frac{7.8}{205} = 3.8 \times 10^{-2}$
$D = 2.2 \times 10^{-7}$
$\sigma_{10} = \frac{7.2}{185} = 3.9 \times 10^{-2}$
$D = 2.5 \times 10^{-7}$
D_2O FED LB.
H_2O FED LB.
250
240
230
220
210
200
190
180
230
220
210
200
190
180
170
0.1
1
10
50
90
99
99.9
D_2O IN EFFLUENT wt.%

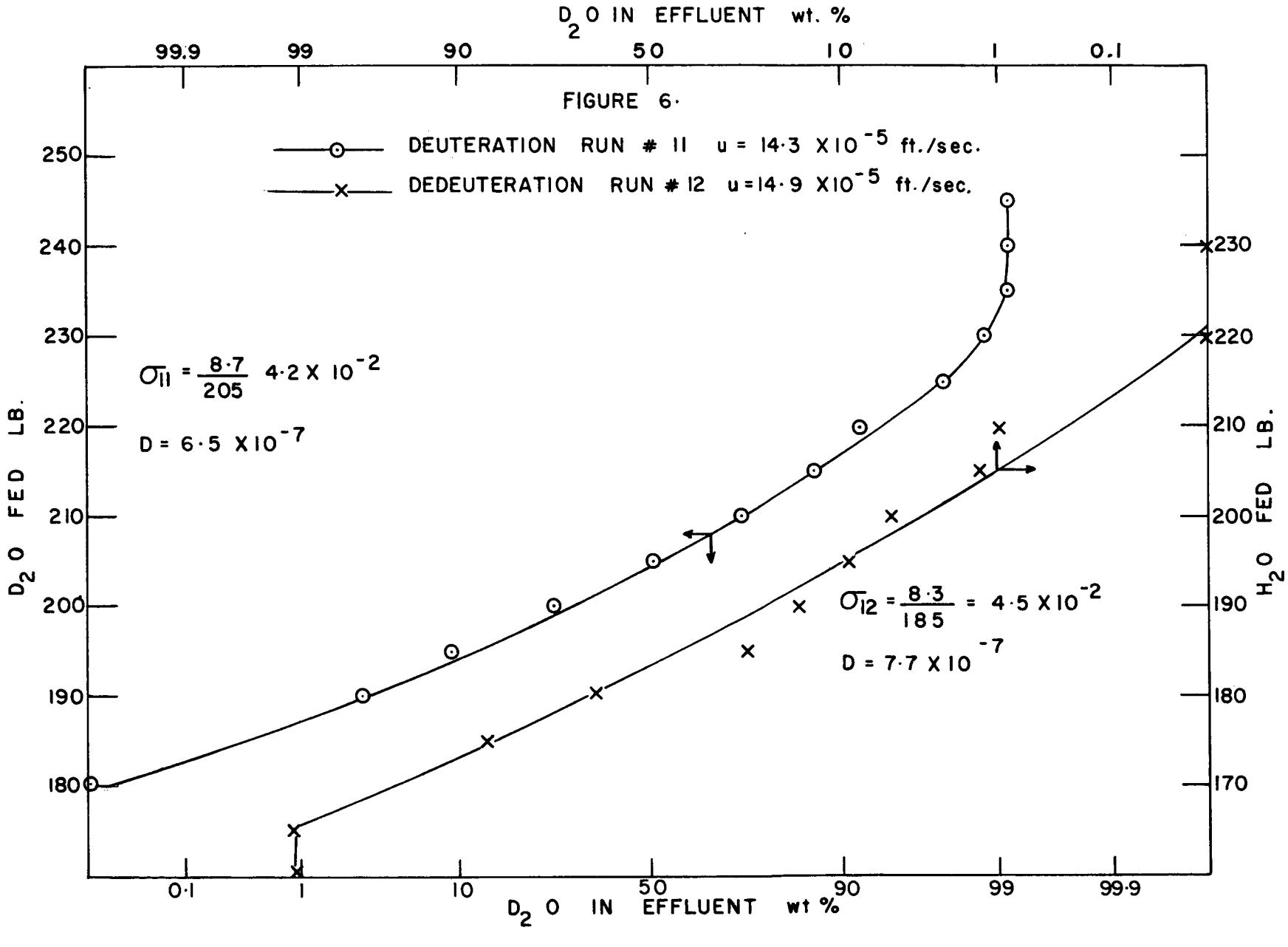

D2O IN EFFLUENT wt. %
99.9
99
90
50
10
1
0.1
DEUTERATION RUN # 11 u = 14·3 X10-5 ft./sec.
DEDEUTERATION RUN # 12 u=14·9 X10-5 ft./sec.
σ11 = 8·7/205 4·2 X 10-2
D = 6·5 X10-7
σ12 = 8·3/185 = 4·5 X10-2
D = 7·7 X10-7
D2O FED LB.
H2O FED LB.
250
240
230
220
210
200
190
180
230
220
210
200
190
180
170
0·1
1
10
50
90
99
99·9
D2O IN EFFLUENT wt %

FIGURE 6·

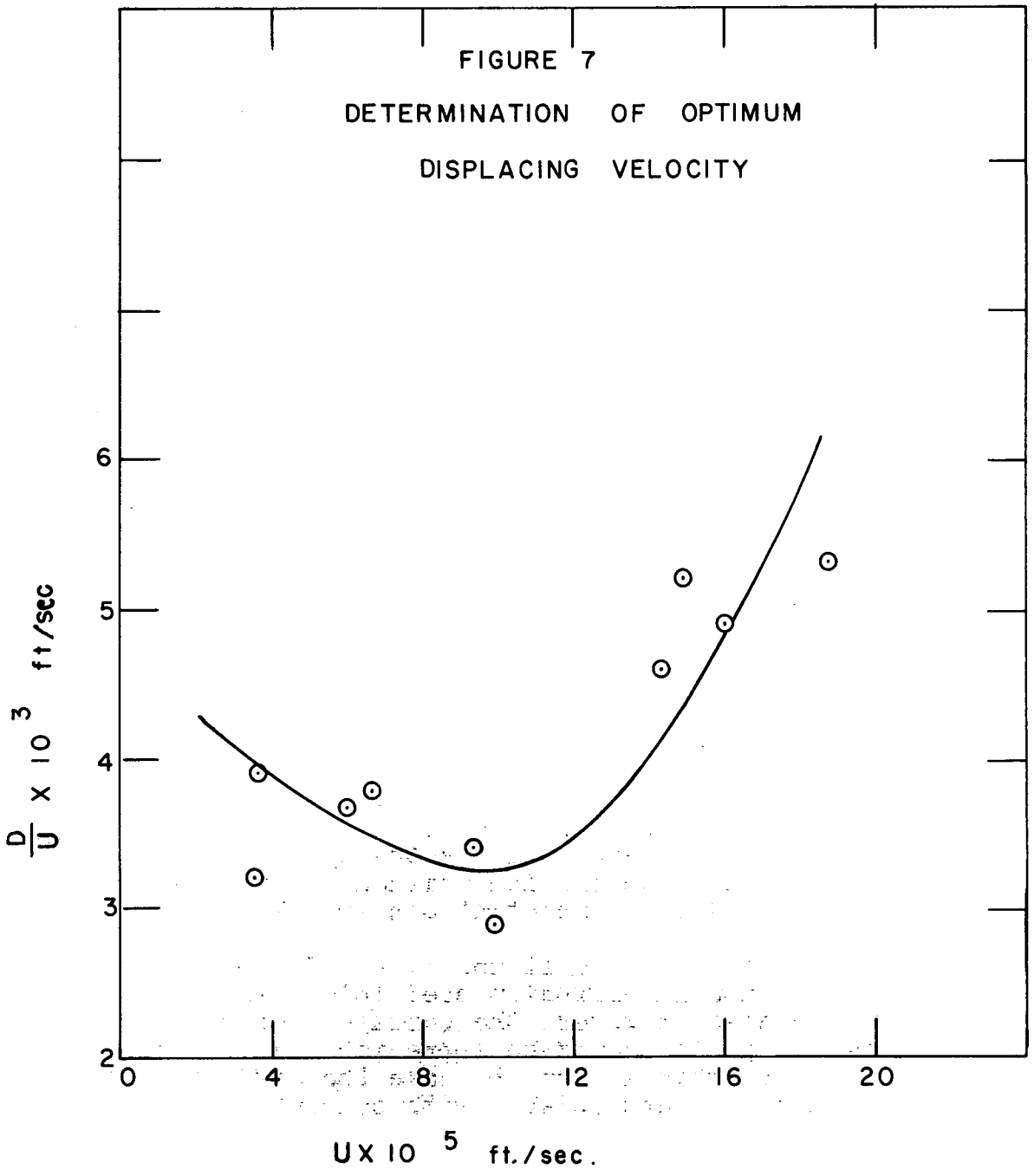


FIGURE 7
DETERMINATION OF OPTIMUM
DISPLACING VELOCITY
$\frac{D}{U} \times 10^3$ ft/sec
6
5
4
3
2
0
4
8
12
16
20
U X 10 5 ft./sec.

The cost per cycle are plotted against displacing velocity in Figure 8.

Calculated longitudinal dispersion coefficients (D) are plotted against

$\left(d_p \cdot \frac{U}{e}\right)$ in Figure 9.

The dotted line shown was calculated from the equation:

$$D = 2.92\, d_p \left(\frac{U}{e}\right)^{1.08}$$

DISCUSSION

The first part of this discussion is aimed at justifying the treatment of the data.

Both the diffusion model of Levenspiel and Smith and the mixing cell model of Aris and Amundson indicate that the lines in Figure 2-6 should be straight. There is however some curvature.

Because both natural water and reactor grade D_2O contain D_2O and H_2O respectively, the figures used on the concentration scale should be:

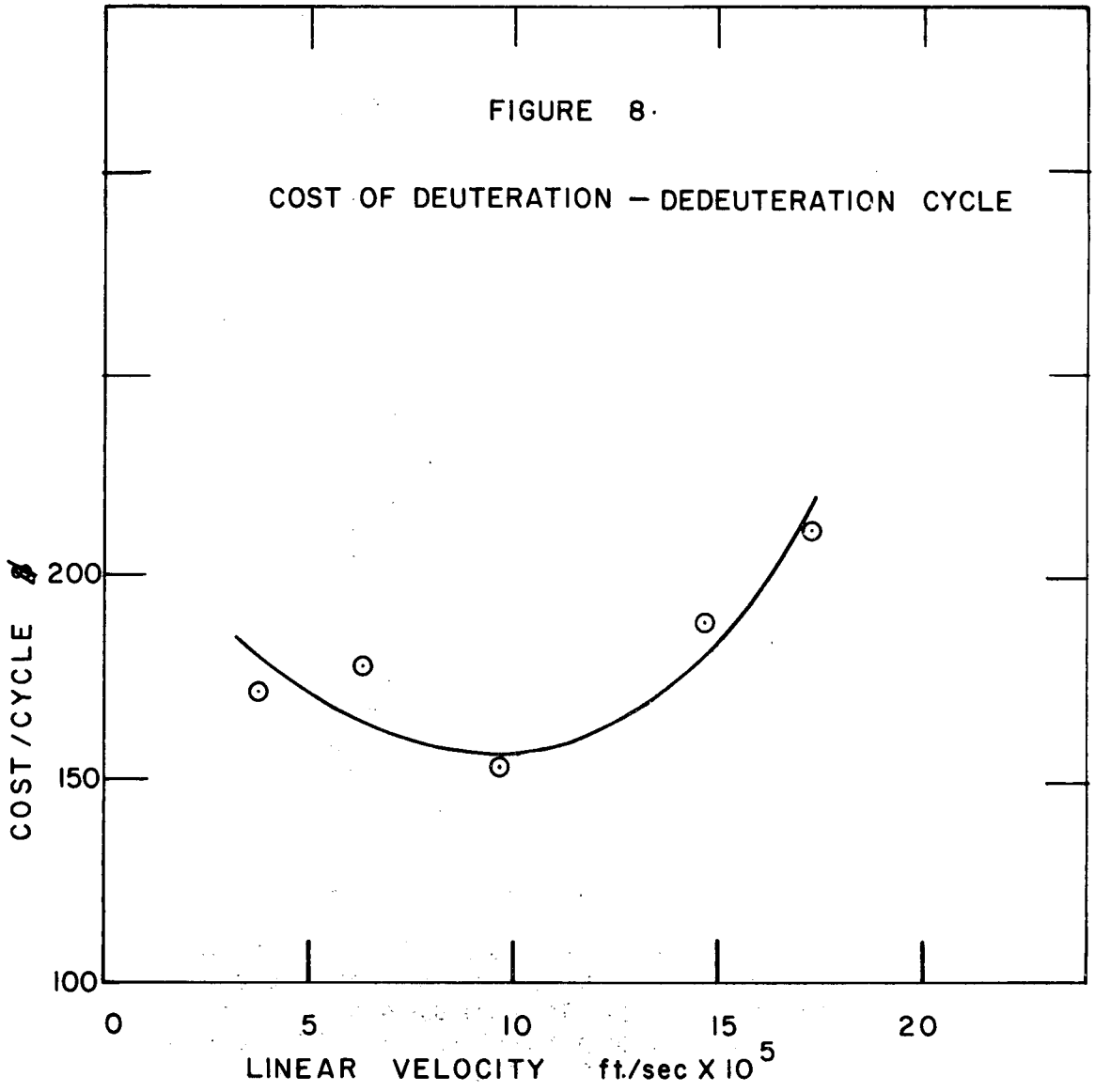
$$\frac{\text{wt \% } D_2O \text{ in effluent}}{\text{wt \% } D_2O \text{ in } D_2O \text{ used} - \text{wt \% } D_2O \text{ in } H_2O \text{ used}} \times 100$$

Use of these modified concentration figures has the effect of flattening the ends of the curves. Straight lines do in fact result at the lower displacing velocities. Using the probability paper plots to determine σ and hence D is thus justified for the lower rates. Since the derived value of is unaffected by the concentration units used the analytical data rather than modified concentrations are plotted.

The curvature found at the higher flowrates could be caused by a variation in diffusion coefficient with concentration. If this were the case, however, the curvature of the deuteration and dedeuteration plots should be appreciably different on the plots shown. Since this is not the case the diffusion coefficient probably does not vary appreciably with concentration.

FIGURE 8.

COST OF DEUTERATION – DEDEUTERATION CYCLE



The mathematical model used to derive equation (1) assumes no retention of fluid by the bed particles themselves. In actual fact the ions of the light and heavy water associated with the resin particles are chemically bound to the resin molecules. If the exchange of ions of the displacing fluid with those on the resin particles is slower than the mixing by eddy diffusion curvature will result. The relative magnitude of these effects should be indicated by the departure of the data of this investigation from the correlation of Ebach and White. It might be expected that agreement would be better at the lower flow rates. Figure 9 indicates that this is the case.

It may be concluded that the method of Levenspeil and Smith is satisfactory for calculating dispersion coefficients from the concentration profiles obtained.

Since the data is adequately represented by equation 1 the effects of varying the parameters of this equation can be predicted.

The length of column used in the calculation of D from $\frac{De}{UL}$ was the total length from inlet to outlet. Of this 34" only 22" were packed with resin. The fact that the use of the total length gives good agreement with previous work indicates that mixing in the end zones of the column is of the same degree as that occurring in the packed section. Since $\sigma \propto \frac{1}{\sqrt{L}}$ a reduction in σ can be obtained either by reducing the length of the end sections or by locating the resin bed supports closer to the ends of the column. These modifications might result in a saving of 15% in the cost of a deuteration - dedeuteration cycle. Before such modifications are considered it would be advisable to study the effects of cartridge end design.

If a number of columns are to be deuterated the amount of D_2O used can be reduced by deuterating in series. Since $\sigma \propto \frac{1}{\sqrt{L}}$, for similar columns in series σ_n will vary with $\frac{1}{\sqrt{n}}$. But the amount of D_2O downgraded varies with $n\sigma_n$, hence the amount of D_2O downgraded will be a function of $\sqrt{n}$. For a four column system the D_2O downgraded for deuteration in series is half the amount for deuteration separately. A similar saving could be achieved by dedeuterating in series.

It is to be noted that the optimum displacing velocity of 10^{-4} ft/sec predicted by Figure 7 is in good agreement with the velocity giving the lowest cost per cycle shown in Figure 8.

The results of this work are compared with those previously reported deuteration and dedeuteration studies in Figure 10.

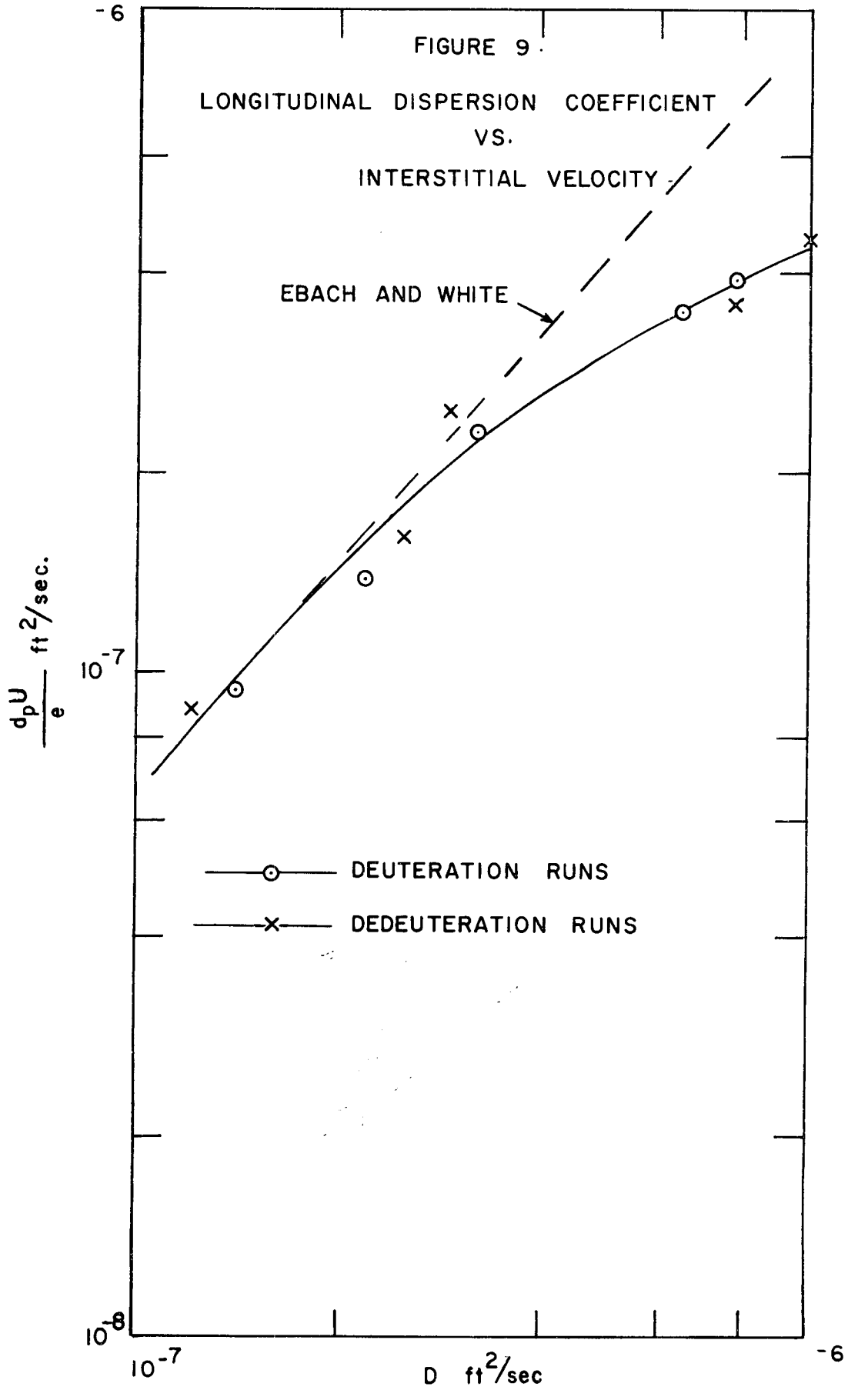


FIGURE 9
LONGITUDINAL DISPERSION COEFFICIENT
VS.
INTERSTITIAL VELOCITY
EBACH AND WHITE
DEUTERATION RUNS
DEDEUTERATION RUNS
$\frac{d_p U}{e}$ ft^2/sec.
D ft^2/sec
10^{-6}
10^{-7}
10^{-8}
10^{-7}
10^{-6}

FIGURE 10

COMPARISON WITH PREVIOUS WORK

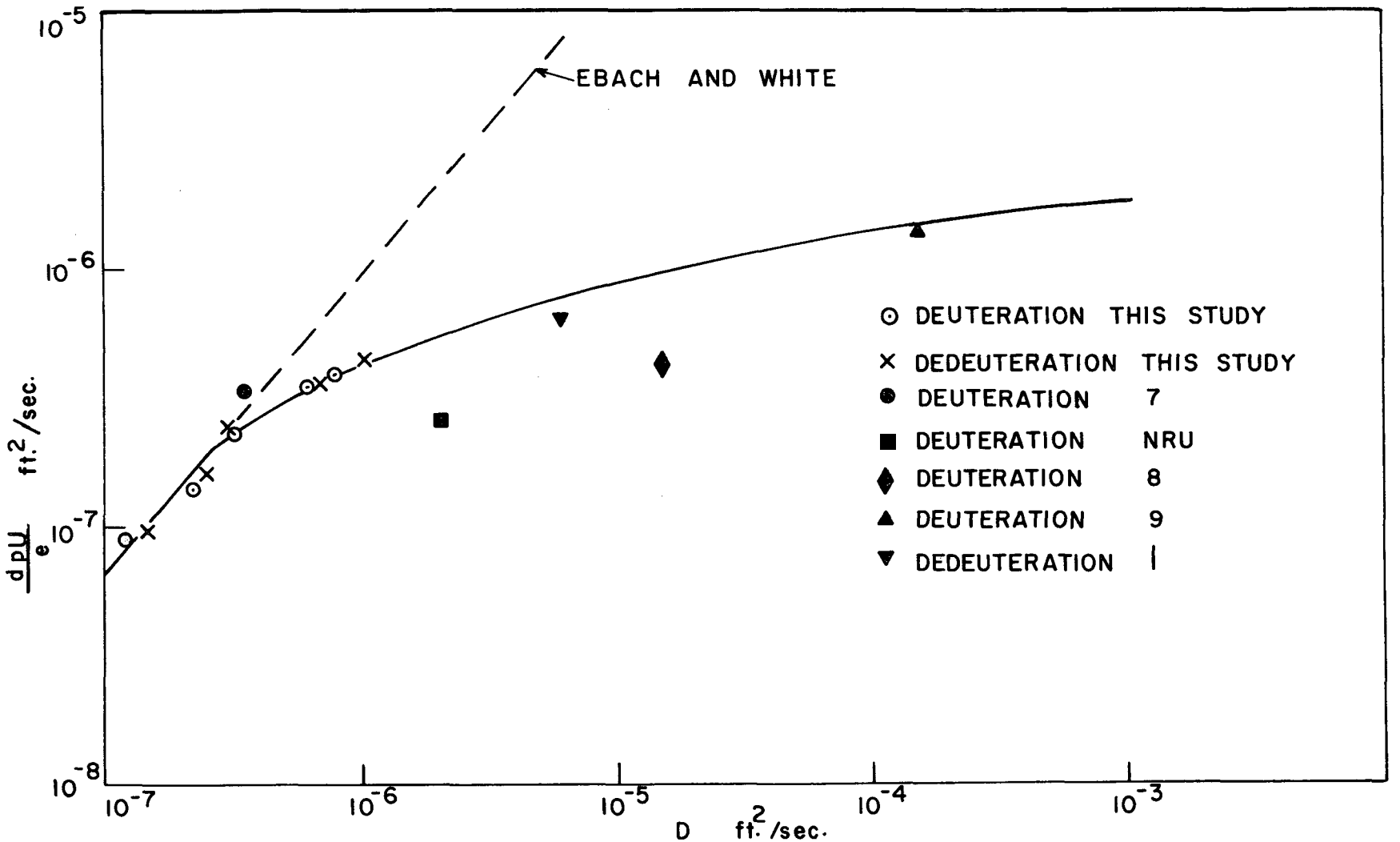
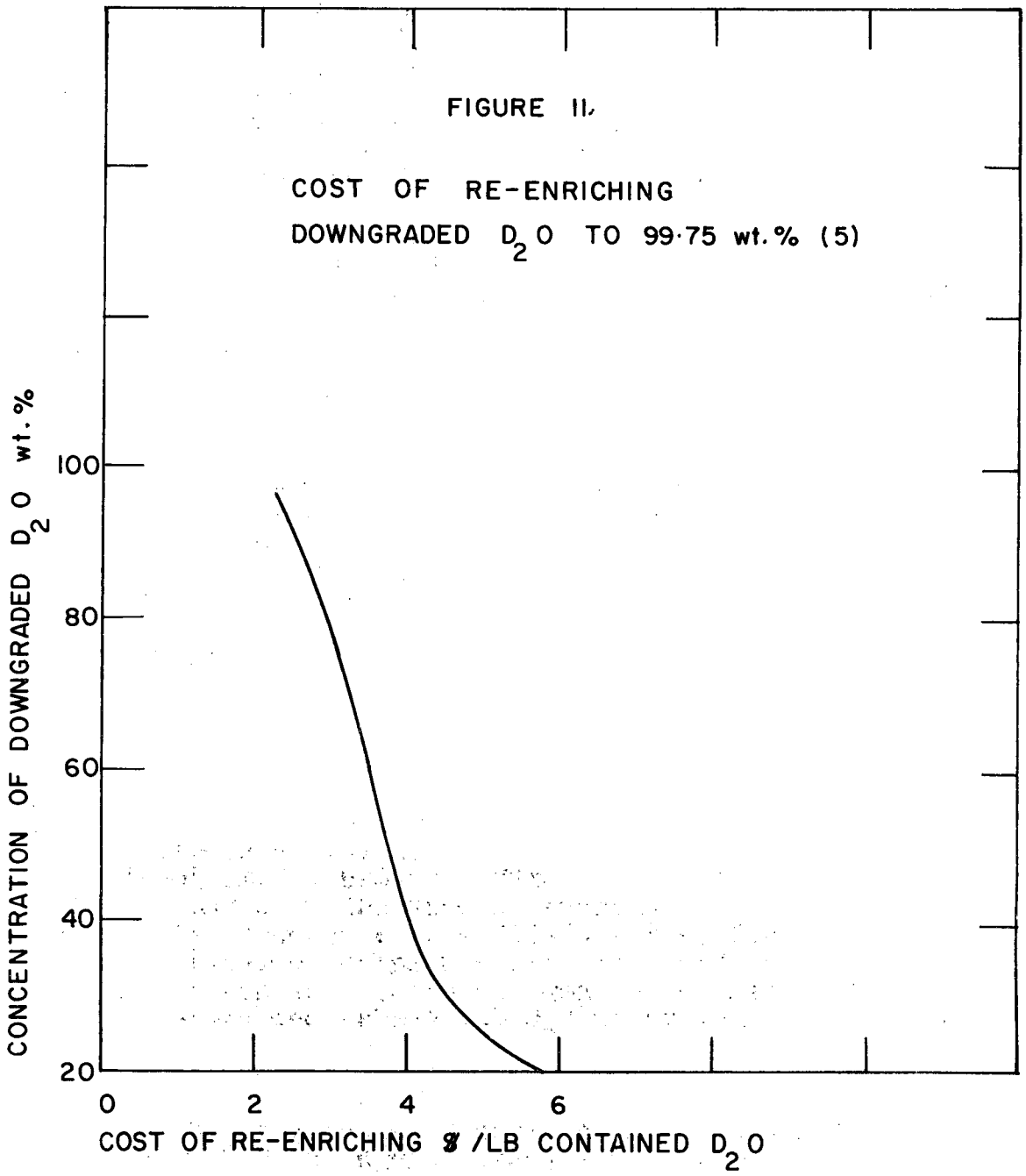


FIGURE II.

COST OF RE-ENRICHING DOWNGRADED D_2O TO 99·75 wt.% (5)



Data in reference 7 was obtained in a 4" column with tapered ends. This data is in good agreement with the data of this investigation. The data of reference 9 were obtained with a similar column. If the assumption is made that, because of similarity of design between the columns of references 7 and 9, the location of the point from reference 9 is due to velocity effects only it can be concluded that the deviation of the points from the three remaining references is due to undesirable design features. These points are taken from data on industrial columns with sharp changes in cross section at the ends. In the case of the NRU column the resin cartridge is contained in a concentric tank and leakage of D_2O through the annulus occurs.

The disagreement between these three points and the data of this investigation may be taken as an indication of stagnant pockets in the three columns.

Agreement between the data of this investigation and the data from laboratory columns as well as data from other systems (Ebach and White) is a good indication of the correctness of the design used in this study.

If for any reason it should become desirable to use resin of a different mean particle size, the longitudinal dispersion could be determined from Figure 10. Knowing the length of the column, the void fraction of the resin bed and taking an optimum displacing velocity of 10^{-4} ft/sec $\frac{De}{UL}$ could be calculated. σ could then be calculated from the equation:

$$\sigma = \sqrt{\frac{2\ De}{UL}}$$

Multiplication of this value of by the void volume of the column will give a value in volume units. A straight line drawn on probability paper with the void volume located at 50% concentration and with shope corresponding to the calculated value of in volume units will give a theoretical displacement profile. While this line will not agree perfectly with experimental curves for either deuteration of dedeuteration, it will give the quantity of D_2O downgraded per cycle.

CONCLUSIONS

1. The optimum superficial linear velocity for deuteration and dedeuteration of a resin column is 10^{-4} ft/sec (0.36 ft/hr).

2. The cost of upgrading the heavy water downgraded in a deuteration - dedeuteration cycle for a single NPD-2 column at the optimum velocity is $150.

3. The cost can be reduced to $75/cycle if 4 columns are treated in series.

4. A further reduction of approximately $20/cycle could be achieved by modification of the cartridge ends.

5. The elimination of stagnant pockets by suitable design will reduce the quantity of D_2O downgraded in deuteration and dedeuteration operations.

6. The results of this study can be used to predict the quantity of D_2O downgraded in a deuteration - dedeuteration cycle in columns of other geometries and bed particle characteristics.

ACKNOWLEDGMENTS

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NOMENCLATURE

C	Concentration of displacing fluid in effluent	wt %
D	Longitudinal dispersion coefficient	ft^2/sec
d_p	Particle size of packing	ft
e	Void fraction of packing	-
L	Length of column	ft
N	Number of columns in series	-
U	Superficial linear velocity of fluid	ft/sec
$\frac{U}{e}$	Interstitial linear velocity of fluid	ft/sec
V	Volume of column	ft^3
v	Volumetric flow rate of Fluid	ft^3/sec
θ	Time	sec
	Standard deviation of distribution function for single column	-
n	Standard deviation of distribution function for n columns in series	