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ION EXCHANGE MEMBRANE PROCESSES

R. M. WALLACE

SAVANNAH RIVER LABORATORY
E. I. DU PONT DE NEMOURS AND CO.
AIKEN, SOUTH CAROLINA

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ION EXCHANGE MEMBRANE PROCESSES

Techniques were developed and promising preliminary tests were completed in an exploratory study of the applicability of ion exchange membrane processes to such chemical operations as the separation of plutonium from uranium, the separation of americium from curium, the isolation of individual rare earths, the removal of strontium from process waste streams and the continuous concentration of solutions of ions such as Pu^{3+} or Pu^{4+}.

Basis of Membrane Processes

The membrane processes are based on the phenomenon of Donnan membrane equilibrium(1), which, although described in 1924, has not been exploited to a degree commensurate with its apparent technological potential. The Donnan membrane equilibrium is, in general, any thermodynamic equilibrium that is subject to the restraint that some of the species are excluded from portions of the system. In the processes that are being studied in the laboratory, the restraint is imposed by ion exchange membranes, which permit the passage of either cations only or anions only.

If, for example, solutions of electrolytes are placed on opposite sides of a cation exchange membrane the total concentration of electrolyte on each side of the membrane must remain constant because transport of the anions cannot occur. The cations, however, will be redistributed until the following condition of equilibrium is established; a completely analogous expression describes the equilibrium between anions across anion exchange membranes.

$$\left[\frac{C_{iR}^{z+}}{C_{iL}^{z+}}\right]^{1/z} = K \qquad (1)$$

where

C_i^{z+} denotes the activity of i^{th} cation of charge z

R and L refer to solutions on opposite sides of membrane

K is the equilibrium constant

If different concentrations of an acid and a salt of a common noncomplexing anion are placed on opposite sides of a cation exchange membrane, Equation 1 shows that, at equilibrium,

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(1) Donnan, F. G. Chem. Rev. 1, 73 (1924).

$$\frac{C_R^{z+}}{C_L^{z+}} = \left[\frac{H_R^+}{H_L^+}\right]^z \qquad (2)$$

The principal previous applications of the Donnan equilibrium principle have been in constructing membrane electrodes and determining activity coefficients of ions in solution. Although the use of the phenomenon in preparative chemistry has been suggested⁽²⁾, very little work appears to have been done to date.

Considerable interest has been shown in recent years in the development of ion exchange membrane processes for such differing applications as desalination of water and the separation of ions of like charge⁽³,⁴⁾. Most of these applications, however, use electrodialysis, in which ions are forced through membranes by electric fields. In two recent and definitive books on ion exchange and membrane technology only passing mention is made of the Donnan equilibrium⁽⁵,⁶⁾.

Potential Scientific Applications

Measurement of Charges of Ionic Species

Establishment of the charge on an ion is frequently necessary in order to elucidate the structure of the ion. The charge is now determined by one of two methods, both of which are based on measurement of the variation of the distribution coefficient of the ion between an aqueous phase and an ion exchange resin as a function of the concentration of acid in the aqueous phase. In addition, both methods are based on the assumption that the charge on the absorbed ion is identical to that on the unabsorbed ion, and that the

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(2) Sollner, K., et al. "Electrochemical Studies with Model Membranes", pp. 144-88, Ion Transport across Membranes, H. T. Clarke, ed., New York: Academic Press (1954).

(3) Mason, E. A., and W. Juda, "Application of Ion-Exchange Membranes in Electrodialysis", Paper presented at Baltimore meeting of American Institute of Chemical Engineers, Sept. 15-18, 1957.

(4) Katz, W. E. Paper presented at Eighth Annual All-Day Meeting: Separations Processes in Practice, Philadelphia, March 29, 1960.

(5) Helfferich, F. Ion Exchange. McGraw-Hill, New York, 1962.

(6) Tuwiner, S. B. Diffusion and Membrane Technology, Reinhold Publishing Corp., New York, 1962.

activity of the ion in the resin or aqueous phase is proportional to its concentration. Both methods also require that only a small fraction of the absorption capacity of the resin phase be occupied by the ion, so that the assumptions involved in the calculation of charge may be approximately valid. Because this requirement frequently necessitates that measurements be made at high concentrations of acid, the assumptions concerning the constancy of activity coefficients may not be valid.

Charges on ions can be measured by methods based on the Donnan membrane equilibrium without the limitations of the other methods. Equation 2 predicts that the distribution of an ion of charge z between two solutions of different hydrogen ion activity will be equal to the z power of the ratio of the hydrogen ion activities. Measurement of the concentrations of cations and acid on each side of the membrane after equilibrium is established will therefore permit the calculation of z. Because the degree of occupancy of the resin by absorbed cations is unimportant, measurements can be made in solutions that are sufficiently dilute that corrections for variation in activity coefficients can be made by the extended Debye-Hückel theory. This method, furthermore, is free from assumptions concerning the nature of the species absorbed by the ion exchange membrane, and is therefore expected to determine the charge on the ion as it exists in aqueous solutions.

Study of Complex Formation in Solution

The formation of complexes in aqueous solutions is readily studied by potentiometry, spectrophotometry, solvent extraction, and ion exchange. Each of these methods, however, also requires that some property be found by which the change in concentration of the uncomplexed or complexed ion can be measured as a function of the concentration of the ligand. Thus, one must find a reversible electrode, a colored complex, a solvent for the ion, or an ion exchange resin that will provide an easily measured distribution coefficient in desired solutions. The membrane equilibrium method theoretically provides a means for studying complex formation that is applicable to any ion that will pass through a membrane.

The activities in Equations 1 and 2 are those of the free ion in solution. When an ion is complexed, its activity is diminished. If different anions, one of which complexes a specific cation while the other does not, are placed on opposite sides of a cation membrane the cation will become concentrated in the solution containing the complexing anion. Measurement of the distribution of the cation between complexing and noncomplexing media will therefore permit the determination of the equilibrium constant for formation of the complex.

Potential Technological Applications

Separation of Ions

The same property that permits the determination of charges on ions is expected also to permit the separation of ions of different charge. Similarly, the property that permits the study of complex formation is expected also to permit the separation of ions based on their ability to be complexed by specific anions.

The phenomenon of the Donnan membrane equilibrium permits the design of solvent extraction processes in which both phases are aqueous, and which therefore have the potentially great advantage that the specificity of the extractant can be varied at will by a suitable choice of complexing agents.

The types of processes possible with this kind of system are virtually limitless. The following are a few examples:

Separation of rare earths, based on differences in complexing with EDTA

Removal of Sr from $NaNO_3$, based on complexing with EDTA or oxalate

Separation of Am from Cm, based on differences in complexing with α-hydroxyisobutyrate

Separation of UO_2^{2+} from Pu^{4+}, based on difference in charge

Concentration of Highly Charged Ions

A further potential application of the membrane equilibrium principle is to the continuous concentration of highly charged ions such as Pu^{3+} or Pu^{4+}. If the concentrations of acid on opposite sides of a membrane are 0.1 and 1M, the distribution coefficient in favor of the more concentrated acid solution is 1,000 for Pu^{3+} and 10,000 for Pu^{4+}. The use of countercurrent equipment would therefore permit the transfer of all of the plutonium to the more concentrated acid solution, with a very large factor of concentration. The countercurrent equipment would consist simply of a stack of membranes and spacers, and would have no moving parts.

Laboratory Tests

Initial laboratory tests had the objectives of developing techniques for studying membrane equilibrium phenomena with commercially available ion exchange membranes, and developing methods for measuring the charges on ions.

Techniques

The preliminary laboratory apparatus contains two 3- x 3- x 0.5-inch blocks of "Teflon"*, each containing a cylindrical cavity 2 inches in diameter and 0.4 inch deep, with a threaded filling passage leading from the cavity to an edge of the block. A 2.5-inch-diameter circular cation exchange membrane, "Ionac MC3142"**, with two neoprene gaskets, is placed between the two cavities and the blocks are bolted together. The volume of the cavity on each side of the membrane is approximately 20 ml.

In operation, 15 ml of solution is placed in the cavity on each side of the membrane, the threaded filling passages are sealed, and the assembly, with the membrane in a vertical plane, is rotated about an axis through the center of the membrane and normal to its surface, at ~120 rpm. This continuous rotation of the membrane agitates the solutions and keeps the surfaces of the membrane continually in direct contact with the homogeneous aqueous phases.

The initial device for rotating the assemblies can hold the six assemblies that have been constructed to date, and can be operated only at room temperature. A new device will permit the equilibrations to be made in a constant temperature bath.

In preliminary tests to determine the integrity of the membranes, solutions containing 1M $HClO_4$ were placed on one side of the membrane and pure water was placed on the other side. No detectable change in the pH of the water was found after the assemblies had been rotated for 2 hours. This test demonstrated that the membranes did not leak, and also that the rate of transfer of anions through the membranes was extremely (and adequately) slow.

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*Du Pont's trademark for its fluorocarbon plastic.

**Trademark of Ionac Chemical Co.

Measurements

Measurements were made of the distribution of Na^+, Ca^{2+}, Mg^{2+}, and La^{3+} between solutions of perchloric acid of varying concentrations. Perchloric acid was used because it does not form complexes with the test cations. The results of these measurements agreed closely with theory. As described in the following paragraphs, values of the charge on each of the ions were calculated from the ratio between the concentration of the ion and that of hydrogen ion on either side of the membrane; discrepancies between the calculated values and the known values can be attributed to differences among the activity coefficients of ions of different charge in media of the same ionic strength.

The measurements were made by placing a solution of 0.1M $HClO_4$ on one side of the membrane, and a 0.01M solution of the perchlorate salt of the test cation in varying concentrations of $HClO_4$ on the other side, in each of the six membrane cells. The concentration of acid on the side initially containing the salt was usually between 0.01 and 0.1M. The assemblies were rotated for 20 hours at room temperature, and the solutions were sampled and analyzed for hydrogen ion and for the test cation. The preliminary tests indicated that the half time for transfer of sodium ion and calcium ion was about 5 and 30 minutes, respectively; 20 hours was therefore selected as an ample time for reaching equilibrium.

Some tests were also made in which the salts were added to the high acid side of the membrane so that equilibrium was approached from the opposite direction. Substantially the same end points were obtained from the two types of tests. The agreement showed that equilibrium had been established.

The results of the measurements are shown in the following table. The first column in the table contains the ratio, at equilibrium, of the concentration of the cation on the high acid side of the membrane to that on the low acid side. The second column contains the corresponding ratio of hydrogen ion concentrations. The third and fourth columns contain the apparent charge z' and the quantity β (defined in the following Equation 4), which is a measure of the deviation of the system from "ideality".

When Equation 2 is written in terms of concentrations it becomes

$$\left[\frac{C_R}{C_L}\right]\left[\frac{\gamma_{CR}}{\gamma_{CL}}\right] = \left[\frac{H_R}{H_L}\right]^z \left[\frac{\gamma_{HR}}{\gamma_{HL}}\right]^z \qquad (3)$$

where γ is the activity coefficient of the respective ion. Equation 3 can be rearranged to

$$\left[\frac{C_R}{C_L}\right] \Bigg/ \left[\frac{H_R}{H_L}\right]^z = \left[\frac{\gamma_{HR}}{\gamma_{HL}}\right]^z \left[\frac{\gamma_{CL}}{\gamma_{CR}}\right] \equiv \beta \qquad (4)$$

The expression on the right of Equation 4 involving the activity coefficients is defined as β. If all the activity coefficients were unity, or if $\gamma_H{}^z/\gamma_C$ were constant for all concentrations, β would be unity.

Equation 3 can be rearranged as follows

$$\frac{\log\,(C_R/C_L)}{\log\,(H_R/H_L)} = z + \frac{\log\,\beta}{\log\,(H_R/H_L)} \equiv z' \qquad (5)$$

in which z' is defined as the apparent charge on the ion derived from the ratio of concentrations. If β is close to unity, z' will be nearly equal to the actual charge z. The accuracy in the determination of z' will be greater for large ratios of H_R/H_L than for ratios close to unity, because the left side of Equation 5 becomes indeterminate when this ratio is unity.

The data in the following table show that the values of z' are nearly equal to the known charges of the ions in question. The variations in β with the ionic strength of the solutions is in the direction, and of the same order of magnitude, indicated by the equation of Davies, Jones, and Monk(7) for predicting the activity coefficients of ions in solution. The agreement is not complete, and further measurements are being made to develop a better correlation between β and ionic strength, after which measurements will be made of the distribution of other ions between solutions containing various concentrations of perchloric acid. These ions will include Th^{4+}, Zr^{4+}, Al^{3+}, $UO_2{}^{2+}$, Sr^{2+}, and K^+.

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(7) Davies, C. W., H. W. Jones, and C. B. Monk. Trans. Faraday Soc. 48, 921 (1952).

Distribution of Ions between Solutions Containing Various Concentrations of Perchloric Acid

Distribution of Na^+

Na_R/Na_L	H_R/H_L	z'	β
7.95	7.23	1.05	1.10
3.60	3.38	1.07	1.07
2.56	2.40	1.07	1.07
1.80	1.62	1.22	1.11
1.27	1.29	0.94	0.984
1.07	1.06	0.80	1.00

Distribution of Mg^{2+}

Mg_R/Mg_L	H_R/H_L	z'	β
13.92	3.23	2.24	1.33
7.47	2.50	2.19	1.20
4.66	2.05	2.14	1.11
4.53	2.02	2.15	1.11
2.83	1.66	2.09	1.04
1.36	1.17	1.96	0.993

Distribution of Ca^{2+}

Ca_R/Ca_L	H_R/H_L	z'	β
7.57	2.65	2.08	1.08
4.50	2.12	2.00	1.00
3.37	1.73	2.21	1.13
2.41	1.51	2.13	1.06
1.55	1.21	2.29	1.06
1.03	1.02	1.48	0.99

Distribution of La^{3+}

La_R/La_L	H_R/H_L	z'	β
20.48	2.49	3.31	1.33
10.91	1.99	3.47	1.38
7.81	1.82	3.43	1.30
5.42	1.61	3.54	1.30
4.77	1.56	3.51	1.26
3.46	1.43	3.48	1.18
1.95	1.20	3.66	1.13
1.26	1.06	3.81	1.06

ION EXCHANGE MEMBRANE STUDIES

The development of a method for measuring the charge on ions in solution by Donnan equilibrium across ion exchange membranes was completed. The apparent ionic charge is calculated from the equilibrium concentrations of the ion on the opposite sides of the membrane and an activity coefficient correction is then used to derive a more precise value.

The method was verified by measurements of the distribution of eight cations of known charge between solutions of perchloric acid of different concentrations. The usefulness of the method was then demonstrated by similar measurements with Ru(IV) in which the charge per ion was shown to be 4+ rather than 2+. The basis for the method and the experimental data are summarized in the following paragraphs. The experimental technique was described in the May report.

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Ion exchange membranes permit the passage of only cations or anions. When solutions of a noncomplexing acid, such as perchloric acid, are situated on opposite sides of a cation exchange membrane and a cation C with charge Z is introduced into the system the conditions for equilibrium are

$$\frac{\left(C_R^{Z+}\right)}{\left(C_L^{Z+}\right)} = \left[\frac{\left(H_R^+\right)}{\left(H_L^+\right)}\right]^Z \tag{1}$$

where the quantities (C^{Z+}) and (H^+) denote the activities of the cation and hydrogen ion respectively and the subscripts R and L denote the respective sides of the membrane.

When written in terms of concentrations and rearranged, Equation (1) becomes

$$\frac{C_R}{C_L} = \left[\frac{H_R}{H_L}\right]^Z \left[\frac{\gamma_{H_R}}{\gamma_{H_L}}\right]^Z \left[\frac{\gamma_{C_L}}{\gamma_{C_R}}\right] = \beta \left[\frac{H_R}{H_L}\right]^Z \tag{2}$$

where the symbols C and H denote the concentrations of the cation and hydrogen ion respectively, γ denotes the activity coefficients, and β is defined as the product of the activity coefficient terms.

Equation (2) can be rearranged as follows

$$\frac{\log\left(C_R/C_L\right)}{\log\left(H_R/H_L\right)} = Z + \frac{\log \beta}{\log\left(H_R/H_L\right)} \equiv Z' \tag{3}$$

in which Z' is defined as the apparent charge on the ion derived from the ratio of concentrations. Thus, Z' is equal to Z when β is unity. The measurements described in the May report indicated that the difference between Z' and Z is small for singly charged ions but increases sufficiently for larger values of Z to require that corrections be made in applying the method to highly charged ions. Such corrections require an estimation of the value of β.

Values of β were estimated on the basis of assumptions that the activity coefficients γ of all ions in dilute solutions with ionic strength μ less than 0.2M are functions only of μ and Z, and that the value of γ for an ion of charge $(Z > 1)$ is equal to the Z^2 power of the value of γ for an ion of charge $(Z = 1)$:

$$\gamma_Z = \left[\gamma_{Z=1}\right]^{Z^2} \tag{4}$$

These assumptions represent an approximation to the following extended Debye-Huckel formula for the calculation of activity coefficients

$$-\log \gamma = \frac{Z^2 S \sqrt{\mu}}{1 + A \sqrt{\mu}}$$

in which the constants A and S are respectively dependent and not dependent on the nature of the solute. Although the assumption in Equation (4) that the constant A has the same value for all ions in the same medium is not strictly valid, it is the least restrictive assumption that can be applied to all ions. On the basis of these assumptions

$$\beta = \left[\frac{\gamma_{H_R}}{\gamma_{H_L}}\right]^{-Z(Z-1)} \qquad (5)$$

On the basis of the assumption that γ_H is a function only of ionic strength the value of γ_H is equal to that of the mean activity coefficient $\gamma_\pm$ of solute-free perchloric acid at an ionic strength equal to the total ionic strength of the salt-containing solution. As an over-all result of the foregoing assumptions Equation (3) is rearranged to

$$Z = Z' + Z(Z-1) \frac{\log\left({}^{\gamma}H_R/{}^{\gamma}H_L\right)}{\log\left(H_R/H_L\right)} \qquad (6)$$

Under certain conditions a more simplified calculation can be used. The activity coefficient of perchloric acid was found empirically to be related to concentration in solutions whose ionic strength is between 0.02 and 0.2 by the equation

$$\log \gamma = K \log(HClO_4) + B$$

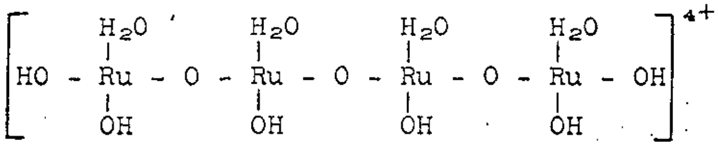
in which K and B are constants and K = -0.055. Consequently, if the distribution measurements are made in the specified region of ionic strength, and if the concentration of solute is sufficiently small that it does not affect the ionic strength, Equation (6) is simplified to

$$Z = Z' - 0.055\, Z(Z-1) \qquad (7)$$

Measurements of the distribution of UO_2^{2+}, Sr^{2+}, and Al^{3+} were made by the procedure described in the May report. The procedure was then modified for measuring the distribution of Th^{4+} and Ru(IV), because of the extremely slow rate of transfer of these ions through the membranes. In the modified procedure the membranes were first saturated with Th^{4+} or Ru(IV) ion and the distribution was then determined by placing the saturated membrane between different concentrations of perchloric acid and agitating the solutions. Equilibrium in these systems was obtained after 70 hours.

The results of all of the distribution measurements to date are summarized in the following table. Each of the results in the table is the average of at least four independent measurements. The values of Z in the third column were calculated from Equation (6) with the aid of literature values of activity coefficients for perchloric acid; Equation (7) would have given nearly as good agreement with theory.

The usefulness of the Donnan equilibrium method is illustrated by the result for Ru(IV). Previous measurements of ion exchange distribution by other workers had indicated a charge of 2+ for the Ru(IV) ion, on the basis of which the ion had been formulated as RuO^{2+}. The value of 4+ obtained in the present measurements, together with a newly determined value of 1+ for the charge per atom of ruthenium* indicates that the Ru(IV) ion exists as a tetramer in aqueous solutions. The tetramer can be formulated as follows:



$$\left[\mathrm{HO}-\underset{\mathrm{OH}}{\overset{\mathrm{H_2O}}{\mathrm{Ru}}}-\mathrm{O}-\underset{\mathrm{OH}}{\overset{\mathrm{H_2O}}{\mathrm{Ru}}}-\mathrm{O}-\underset{\mathrm{OH}}{\overset{\mathrm{H_2O}}{\mathrm{Ru}}}-\mathrm{O}-\underset{\mathrm{OH}}{\overset{\mathrm{H_2O}}{\mathrm{Ru}}}-\mathrm{OH}\right]^{4+}$$

This formulation is consistent with values of 4+ for the charge per ion, 1+ for the charge per atom, and 4+ for the oxidation state of ruthenium in the ion, but is not unique in that other structures can be postulated that conform to these values.

The development of the method for determining charges on ions has been completed. Membrane equilibrium methods are now being developed for studying the formation of complex ions in solution.

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* The determination of this value of 1+ for the charge per atom, which also differs from the values obtained by other investigators, will be described in the October report.

Determination of Ionic Charge by Membrane Equilibrium

	Z'	Z
Na^+	1.07	1.07 ±0.06
Mg^{2+}	2.13	1.99 ±0.05
Ca^{2+}	2.14	2.01 ±0.04
UO_2^{2+}	2.16	2.05 ±0.02
Sr^{2+}	2.16	2.04 ±0.02
La^{3+}	3.54	3.02 ±0.09
Al^{3+}	3.57	3.15 ±0.07
Th^{4+}	4.59	3.95 ±0.09
Ru(IV)	4.76	4.05 ±0.08

MEMBRANE EQUILIBRIUM STUDIES

Formation Constant for UO_2SO_4

The techniques of Donnan equilibrium across ion exchange membranes, which were developed for measuring the charges on ions as described in the October report, were applied to determine the equilibrium constant for formation of the uranyl sulfate complex, UO_2SO_4:

$$UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4$$

The equilibrium constant was found to be 296 ±6 at ionic strength $\mu = 0.1$ and 25°C when expressed in terms of concentrations, and 2500 ±150 when expressed in terms of activities. Day and Powers have reported a value of 76 for the equilibrium constant for concentrations at $\mu = 2.0$ and 25°C, and Ahrland has reported a value of 50 at $\mu = 1.0$ and 20°C(1,2). The differences among the values are probably due to changes in activity of the uranyl and sulfate ions with ionic strength.

Membrane equilibrations were made with the apparatus and techniques described in the May and October reports. Each cation exchange membrane was saturated with uranyl ion and then placed in a cell between 0.1M perchloric acid and a mixture of sulfuric and perchloric acids. The mixed solutions on the "sulfuric acid side" provided various concentrations of sulfate ion at nearly constant ionic strength of 0.10; this sulfate side is referred to as the "right" side in the remainder of this item. The membrane cells were rotated at room temperature (~25°C) for 20 hours and the solution on each side was then analyzed for total acid, sulfate, and uranyl ion. No more than 1% of the sulfate was transferred through the membrane. The equilibrium concentrations are shown in the following table, and are also shown in Figure 2.2 as the right-to-left ratio of uranium concentrations (U_R/U_L) versus total sulfate concentration (S_R).

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(1) R. A. Day, Jr. and R. M. Powers, J. Am. Chem. Soc. 76, 3895 (1954).

(2) S. Ahrland, Acta. Chem. Scand. 5, 1151 (1951).

Concentrations at Equilibrium, M

	Uranium UO_2^{2+} and UO_2SO_4		Total Acid H^+ and HSO_4^-		Sulfate HSO_4^-, SO_4^{2-}, and UO_2SO_4
Expt.	Left	Right	Left	Right	Right
1	0.00248	0.00389	0.0954	0.1023	0.00984
2	.00211	.00465	.0965	.1103	.01937
3	.00160	.00578	.0975	.1274	.03917
4	.00144	.00625	.0984	.1354	.0479
5	.00117	.00701	.0982	.1540	.0698
6	.000898	.00813	.0988	.1791	.0967

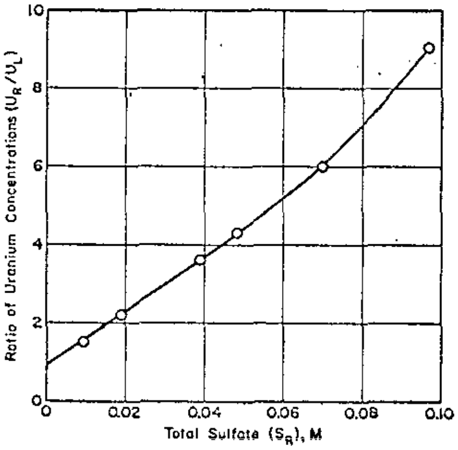

FIG. 2.2 DISTRIBUTION OF URANYL IONS

Calculation of equilibrium constants for this system is complicated by the partial dissociation of the bisulfate ion so that three equilibria must be satisfied simultaneously:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

$$UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4$$

$$\frac{(UO_2^{2+})_R}{(UO_2^{2+})_L} = \left[\frac{(H^+)_R}{(H^+)_L}\right]^2$$

The third expression defines the conditions for Donnan membrane equilibrium in terms of activities; the subscripts R and L refer to the right (sulfate) and left sides of the membrane. In all calculations the uranyl ion was assumed not to be complexed by perchlorate, and perchloric acid was assumed to be completely dissociated, so that U_L and H_L are equal to the concentrations of free uranyl and hydrogen ions on the left side of the membrane, which contained no sulfate.

The calculation of the equilibrium constant involved the simultaneous satisfaction of the following equations. All ionic and molecular formulas in parentheses refer to concentrations of constituents on the sulfate side (R) of the membrane unless otherwise specified by the subscript L. Equations 1 through 3 relate the measured quantities S_R, H_R, and U_R to the concentrations of species in solution. Equation 4 is the membrane equilibrium expression relating the concentrations of UO_2^{2+} and H^+ on the right to those on the left. Equation 5 expresses the acid dissociation constant of the bisulfate ion; K_{A_C} is this constant in terms of concentrations and K_{A_A} is in terms of activities. Equation 6 is the expression for calculating ionic strength. Equation 7 is the Davies expression for calculation of activity coefficients in dilute solutions(3). Equations 8 and 9 are the expressions for the formation constants of the uranyl sulfate complex, in terms of concentrations and activities, respectively.

$$S_R = (HSO_4^-) + (SO_4^{2-}) + (UO_2SO_4) \tag{1}$$

$$H_R = (H^+) + (HSO_4^-) \tag{2}$$

$$U_R = (UO_2^{2+}) + (UO_2SO_4) \tag{3}$$

$$\frac{(UO_2^{2+})}{(H^+)^2} = \frac{U_L}{H_L{}^2}\left[\frac{\gamma_{H_R}}{\gamma_{H_L}}\right]^2\left[\frac{\gamma_{UO_{2_L}}}{\gamma_{UO_{2_R}}}\right] \tag{4}$$

$$K_{A_C} = \frac{K_{A_A}\gamma_{HSO_4^-}}{\gamma_{H^+}\gamma_{SO_4^{2-}}} = \frac{(SO_4^{2-})(H^+)}{(HSO_4^-)} \tag{5}$$

$$\mu_R = \tfrac{1}{2}\sum C_i Z_i{}^2 = (H^+) + 3(UO_2^{2+}) + (SO_4^{2-}) \tag{6}$$

$$-\log \gamma_i = 0.5\ Z_i{}^2\left[\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\ \mu\right] \tag{7}$$

$$K_{U_C} = \frac{(UO_2SO_4)}{(UO_2^{2+})(SO_4^{2-})} \tag{8}$$

$$K_{U_A} = \frac{K_{U_C}}{\gamma_{SO_4}\gamma_{UO_2}} \tag{9}$$

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(3) W. C. Davies, H. W. Jones, and C. B. Monk, *Trans. Faraday Soc.* *48*, 921 (1952).

The constants K_{U_C} and K_{U_A} were calculated by iteration as follows. The ionic strength of all solutions on the right was first assumed to be $\mu = 0.1$, and the activity coefficients were calculated from Equation 7. The acid dissociation constants of bisulfate ion (K_{A_C}) were then evaluated from the value of $K_{A_A} = 0.0103$ reported by Davies, Jones, and Monk$^{(3)}$ and from the calculated values of the activity coefficients. Equations 1 through 5 were then combined to provide a cubic equation in (H^+), and the value thus obtained for (H^+) was then used for calculating the concentrations of all other ions. The ionic concentrations so obtained were then substituted in Equation 6 to obtain a new value of the ionic strength, and the entire procedure was repeated. Only one iteration was necessary to obtain consistent values of the concentrations. The results of these calculations then gave the quantities required for calculating the formation constants K_{U_C} and K_{U_A} from Equations 8 and 9.

The results of the calculations are summarized in the following table, which shows the ionic strength of the solutions, the concentrations and the activity coefficients of the pertinent ions, and the calculated values of K_{U_C} and K_{U_A}. The activity coefficient of the uncharged complex UO_2SO_4 was assumed to be unity in all cases. The average of the values for K_{U_C} is 296 ±6, and that for K_{U_A} is 2500 ±150. The results of the first experiment were excluded from the averages because the data were known to be less precise than those of the other experiments.

Formation of Uranyl Sulfate

	Calculated Values		Equilibrium Concentrations of Species on Right Side of Membrane, M			Formation Constants	
Expt.	μ_R	$\gamma_{SO_4};\gamma_{UO_2}$	$UO_2^{2+} \times 10^3$	$UO_2SO_4 \times 10^3$	$SO_4^{2-} \times 10^3$	K_{U_C}	K_{U_A}
1	0.105	0.357	2.54	1.35	1.96	271	2130
2	.107	.355	2.18	2.47	3.87	293	2330
3	.113	.348	1.73	4.05	8.00	293	2420
4	.115	.339	1.58	4.67	9.82	301	2530
5	.121	.340	1.35	5.66	14.49	289	2490
6	.130	.333	1.16	6.97	19.99	303	2750

The values of K_{U_C} vary only within 2%. Those of K_{U_A} vary within 6%, and generally increase with increasing ionic strength. This increase may be due to limitation of the accuracy of estimation of activity coefficients by Equation 7, or to lack of consideration of the formation of higher sulfate complexes of UO_2^{2+}.

Further experiments are planned, in which the uranium will consist of U^{233} at tracer concentration. This technique will simplify the calculations greatly because the presence of uranyl ion in tracer concentration will not affect the concentration of sulfate, and will allow an estimation to be made of the formation constants of the higher sulfate complexes. To permit the larger variation of sulfate concentration that will be necessary to observe the effect of the higher sulfate complexes, the distribution of UO_2^{2+} will be measured between sodium sulfate-bisulfate mixtures and sodium perchlorate-perchloric acid mixtures.

MEMBRANE EQUILIBRIUM STUDIES

In continuing study to determine the equilibrium constant for formation of the uranyl sulfate complex (UO_2SO_4) by measuring equilibria across ion exchange membranes, a technique was developed that permits the simultaneous determination of the concentration of free sulfate ions as well as the desired equilibrium constant.

The membrane equilibrium method for determining the formation constant requires knowledge of the concentration of free sulfate ions as well as of the distribution ratio of uranyl ion between solutions of perchloric and sulfuric acids. In the method that was used previously to obtain these concentrations, as described in the October report, the equilibrium quotient (the equilibrium constant expressed in terms of concentrations and denoted as K_{A_C} in the October report) was calculated from the accepted literature value of the equilibrium constant for the dissociation of bisulfate ion, K = 0.0102, and from the Davies equation for the estimation of activity coefficients

$$-\log \gamma = Z^2 \left[\frac{0.5\sqrt{\mu}}{1+\sqrt{\mu}} - 0.2\,\mu\right] \qquad (1)$$

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(1) R. N. Parkins and R. Usher, "The Effect of Nitrate Solutions in Producing Stress-Corrosion Cracking in Mild Steel", First International Congress on Metallic Corrosion, pp. 289-295, Butterworths (London) 1961.

The arbitrary nature of Equation 1 suggested that the equilibrium quotient at concentrations as high as 0.05 molar, and hence the value K = 0.0102, might be seriously in error. The new method eliminates the previous uncertainties in the concentrations of the sulfate ion, and simplifies substantially the over-all calculation.

The newly developed method consists of measuring simultaneously the distribution at tracer concentrations, both of uranyl ions (U^{233}) and sodium ions (Na^{22}), between solutions of various concentrations of perchloric acid on one side (L) of the membranes and sulfuric acid on the other side (R). The conditions for equilibrium across a cation exchange membrane require that

$$\frac{(Na)_R}{(Na)_L} = \frac{(H^+)_R}{(H^+)_L}\left[\frac{\gamma_{H_R}}{\gamma_{H_L}}\right]\left[\frac{\gamma_{Na_L}}{\gamma_{Na_R}}\right] \qquad (2)$$

$$\frac{(UO_2^{2+})_R}{(UO_2^{2+})_L} = \left[\frac{(Na)_R}{(Na)_L}\right]^2\left[\frac{\gamma_{Na_R}}{\gamma_{Na_L}}\right]^2\left[\frac{\gamma_{UO_{2_L}}}{\gamma_{UO_{2_R}}}\right] \qquad (3)$$

Knowledge of the distribution of sodium ions between the solutions on the two sides therefore permits the calculation of the concentrations of free hydrogen ions $(H^+)_R$ and uranyl ions $(UO_2^{2+})_R$ in the sulfuric acid solutions. Two assumptions are involved: (1) perchloric acid and uranyl perchlorate are assumed to be completely dissociated, and (2) the ratios of activity coefficients in Equations 2 and 3 are assumed to be unity. Both assumptions can be shown to be nearly valid for sodium and hydrogen ions at ionic strength $\leqslant 0.1$. The first assumption is reasonable also for uranyl ion; the conditions under which the second assumption is valid for uranyl ion are somewhat complicated and will be discussed in detail in a future report.

The remainder of this item is concerned with the determination of a more accurate value of the equilibrium constant K for the dissociation of bisulfate ion.

Sulfuric acid dissociates in two steps

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad (4)$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad (5)$$

The first step is assumed to be complete. The concentration of each constituent in an aqueous solution of sulfuric acid may be obtained from the following equations:

$$(H)_t = (H^+) + (HSO_4^-) \tag{6}$$

$$(S)_t = (HSO_4^-) + (SO_4^{2-}) \tag{7}$$

$$(H^+)_R = \frac{(Na)_R}{(Na)_L} (H^+)_L \tag{8}$$

where $(H)_t$ = total acid concentration, determined by titration to phenolphthalein end point

$(S)_t$ = total sulfate concentration, determined analytically

$(H^+)_R$ = concentration of free hydrogen ion in sulfuric acid

$(H^+)_L$ = concentration of perchloric acid on opposite side of membrane

The results of measurements of the equilibrium quotient Q for dissociation of HSO_4^- in solutions of H_2SO_4 between 0.1 and 0.005M are shown in the following table. The quantities in the first four columns are defined in the preceding paragraph. Q is calculated from the equation $Q = \frac{(H^+)(SO_4^{2-})}{(HSO_4)}$ and α is the degree (or fraction) of HSO_4^- dissociated,

Measurements of Dissociation of HSO_4^-
by Membrane Equilibrium

$(S)_t$	$(H)_t$	$(H^+)_L$	$(Na)_R/(Na)_L$	Q	α
0.0957	0.1951	0.1013	1.24	0.0474	0.270
0.0489	0.0965	0.0494	1.311	0.0353	0.352
0.0499	0.0980	0.0710	0.930	0.0368	0.358
0.0512	0.1029	0.0926	0.739	0.0333	0.327
0.0246	0.0471	0.0241	1.419	0.0312	0.477
0.0250	0.0486	0.0379	0.925	0.0292	0.455
0.0254	0.0493	0.0465	0.761	0.0288	0.449
0.00982	0.01949	0.01040	1.523	0.0268	0.630
0.00990	0.01969	0.01492	1.049	0.0227	0.595
0.01000	0.02043	0.01966	0.815	0.0203	0.559
0.00499	0.00992	0.00523	1.638	0.0231	0.725
0.00503	0.01002	0.00760	1.133	0.0221	0.721
0.00513	0.01018	0.00978	0.877	0.0189	0.687

ie (SO_4^{2-}) divided by the molality M. In the region of concentrations used in the measurements, the molality is virtually equal to the molarity.

Only a single membrane equilibrium was measured at 0.1M H_2SO_4, while three measurements with different concentrations of perchloric acid were made at each other concentration of H_2SO_4. The agreement among each set of three measurements shows that the method is internally consistent and that the assumptions involved in its use are valid.

The degree of dissociation, α, determined by the membrane equilibrium method is compared in the following table with values obtained by Kerker(1) from conductivity measurements and by Young(2) from Raman spectra. In this comparison the most reliable membrane value of α is used (ie the value for which the $(Na)_R/(Na)_L$ ratio of sodium concentrations is closest to unity). The agreement among the three methods is quite good; the Raman spectra provide the least precise values in the region of concentration covered. Although the results obtained by membrane measurements are slightly higher than those obtained by conductivity measurements the agreement provides ample validation of the membrane method. Discrepancies at the lowest concentrations appear to be attributable to lack of attainment of equilibrium.

Comparison with Other Methods

H_2SO_4, M	Degree of Dissociation, α, of HSO_4^- Membrane Equilibrium	Conductivity	Raman Spectra
0.10	0.270	0.266	0.32
0.050	0.358	0.336	0.34
0.025	0.455	0.417	
0.010	0.595	0.523(a)	
0.005	0.721	0.667	

(a) H_2SO_4 = 0.0125M

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(1) M. Kerker, J. Am. Chem. Soc. 79, 3664 (1957).

(2) T. F. Young, et al. "Raman Spectral Investigations", The Structure of Electrolytic Solutions, W. J. Hamer, Editor, p. 35, John Wiley and Sons, New York (1959).

Calculation of the equilibrium constant K for bisulfate dissociation from the equilibrium quotients Q requires knowledge of the activity coefficients γ_i of the ionic species. The activity coefficients are usually obtained by some assumption such as Equation 1 or by choosing some arbitrary value for the distance parameter D in the more precise modified Debye-Huckel equation

$$-\log \gamma_i = \frac{0.509\ Z^2 \sqrt{\mu}}{1 + D\sqrt{\mu}} \qquad (9)$$

where μ = ionic strength

γ_i = activity coefficient of ion

Z_i = charge of ion

The specification of a numerical value for D was obviated however, by making use of literature values of activity data for sulfuric acid, as follows.

Activity data for sulfuric acid were combined with measured values of the degree of dissociation α of bisulfate ion to calculate the true equilibrium constant. The equilibrium constant in terms of activities is

$$K = \frac{A_{H^+} A_{SO_4^{2-}}}{A_{HSO_4^-}} \qquad (10)$$

and the stoichiometric activity A_2 of sulfuric acid, measured potentiometrically, is

$$A_2 = A_{H^+}^2 A_{SO_4^{2-}} \qquad (11)$$

Equations 10 and 11 can be combined to give

$$K = \frac{A_2}{A_{H^+} A_{HSO_4^-}} \qquad (12)$$

Equations 10 and 12 can each be written in terms of the stoichiometric molality M of sulfuric acid, the degree of dissociation α of the bisulfate ion, and the activity coefficients γ_i of the several species

$$K = \left[\frac{M\alpha(1+\alpha)}{1-\alpha}\right]\left[\frac{\gamma_{H^+}\gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}}\right] \qquad (10')$$

$$K = \left[\frac{A_2}{M^2(1+\alpha)(1-\alpha)}\right]\left[\frac{1}{\gamma_{H^+}\ \gamma_{HSO_4^-}}\right] \qquad (12')$$

Equations 10' and 12' can now be combined and written in terms of the stoichiometric mean activity coefficient $\gamma_{\pm}$, because by definition

$$A_2 = 4M^3\gamma_{\pm}^3$$

The foregoing operations yield the following equations

$$\gamma_{H^+}^2\ \gamma_{SO_4^{2-}} = \frac{4\gamma_{\pm}^3}{\alpha(1+\alpha)^2} \qquad (13)$$

$$\gamma_{H^+}\ \gamma_{HSO_4^-} = \frac{1}{K}\ \frac{4M\ \gamma_{\pm}^3}{(1+\alpha)(1-\alpha)} \qquad (14)$$

Division of the cube root of Equation 13 by Equation 14, followed by solution for K, produces the following working equation

$$K = \sqrt[3]{16}\ M\gamma_{\pm}^2 \left[\frac{\alpha}{1+\alpha}\right]^{\frac{1}{3}} \left[\frac{1}{1-\alpha}\right] \left[\frac{\gamma_{SO_4^{2-}}}{\gamma_{H^+}\ \gamma_{HSO_4^-}^3}\right]^{\frac{1}{3}} \qquad (15)$$

All terms on the right of Equation 15, except for the final quotient of activity coefficients, are experimental quantities. If the activity coefficients obey Equation 9 with any single (although unknown) value of the distance parameter D,

$$\gamma_{SO_4^{2-}} = \gamma_{H^+}^4 = \gamma_{HSO_4^-}^4 \qquad (16)$$

and the final quotient of γ_i values in Equation 15 becomes unity. This condition is usually satisfied by most electrolytes for concentrations $\leqslant$0.1M.

Equation 15 was applied to the membrane equilibrium data in the table on page II-18, in conjunction with tabulated values of $\gamma_{\pm}$(3). The calculational results are shown in the following table. (The value of α at 0.02M H_2SO_4 was interpolated.)

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(3) H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, Third Ed. p. 576, Reinhold Publishing Co., New York (1958).

Equilibrium Constant for Dissociation of HSO_4^-

H_2SO_4, M	α	$\gamma_\pm$	K
0.005	0.721	0.639	0.0137
.01	.595	.544	.0132
.02	.488	.453	.0139
.05	.358	.340	.0144
.10	.270	.265	.0144

The average value of the bisulfate dissociation constant K obtained in this manner is 0.0139 ±0.0005, which is considerably higher than the value 0.0102 that is generally accepted. The dissociation data obtained from Raman spectra and conductivity experiments would also lead to values of K considerably higher than 0.0102 if the data were treated similarly. The results at present, therefore, indicate either that the value 0.0102 is too low, probably because improper values of activity coefficients were used to obtain it, or that the literature values for $\gamma_\pm$ are not valid.

Membrane equilibrium measurements of the formation constant of uranyl sulfate are now being made at several temperatures, with use of the foregoing methods for determining the concentration of sulfate and free uranyl ions in the solutions.

MEMBRANE EQUILIBRIUM STUDIES

In continuing study to determine the equilibrium constant for formation of the uranyl sulfate complex

$$UO_2^{2+} + SO_4^{2-} = UO_2SO_4 \qquad (1)$$

by measuring equilibrium conditions across ion exchange membranes, the technique described in the December report was used at 25, 35, and 50°C, and at several values of ionic strength. As expected, the equilibrium concentration quotient Q varies considerably with ionic strength; but the equilibrium ratio K of activities calculated with the Debye-Hückel equation is fairly constant at a given temperature. Average values of K were found to be 1710 at 25°C, 2330 at 35°C, and 3510 at 50°C. From these data the enthalpy change, ΔH, for Reaction 1 was calculated to be +5.48 kcal/mol.

In the membrane equilibrium method, simultaneous measurements are made of the distribution at tracer concentrations of U^{233} uranyl ions and of Na^{22} ions, between solutions of various concentrations of perchloric acid on one side (L) of a membrane of cation exchange resin, and solutions of sulfuric acid or of a mixture of sulfuric acid and sodium bisulfate on the other side (R) of the membrane. The concentration of uncomplexed sulfate ion is derived from analyses of the solutions and the R/L ratio of Na^{22} activities, as described in the December report. The concentration of uncomplexed uranyl ion in the sulfate solution $(UO_2^{2+})_R$ is given by the equation

$$\frac{(UO_2^{2+})_R}{(UO_2^{2+})_L} = \left[\frac{(Na)_R}{(Na)_L}\right]^2 \left[\frac{\gamma_{Na_R}}{\gamma_{Na_L}}\right]^2 \left[\frac{\gamma_{UO_{2_L}}}{\gamma_{UO_{2_R}}}\right] \qquad (2)$$

If the same value of ionic strength is maintained on both sides of the membrane, the activity coefficients are equal so that their ratio is unity. If the values of ionic strength are not identical, a correction for activity coefficients can be applied. Although such corrections will not exceed ~12% for values of ionic strength between 0.1 and 0.2, maintenance of uniform ionic strength is preferred.

Two successive reactions of uranyl ion with sulfate ion can be represented as follows. The third analogous reaction, and possibly additional successive reactions, may also occur.

$$UO_2^{2+} + SO_4^{2-} = UO_2SO_4$$

$$UO_2SO_4 + SO_4^{2-} = [UO_2(SO_4)_2]^{2-}$$

$$[UO_2(SO_4)_2]^{2-} + SO_4^{2-} = [UO_2(SO_4)_3]^{4-}$$

The total uranyl concentration on the sulfate side of the membrane $(UO_2)_R$ is the sum of the concentrations of its various species,

$$(UO_2)_R = (UO_2^{2+})_R + UO_2SO_4 + [UO_2(SO_4)_2]^{2-} + \ldots \qquad (3)$$

When Equation 3 is written in terms of measurable quantities and equilibrium quotients Q_1, Q_2, ..., it becomes

$$(UO_2)_R = (UO_2^{2+})_R[1 + Q_1(SO_4) + Q_1Q_2(SO_4)^2 + \ldots] \qquad (4)$$

where $(UO_2^{2+})_R$ is the concentration of uncomplexed uranyl ion in the sulfate solution. Also, $(UO_2)_L = (UO_2^{2+})_L$ because none of the uranyl ion is complexed in the perchloric acid. If Equation 4 is combined with Equation 2 and the quantity R is defined as

$$R = \left[\frac{(UO_2)_R}{(UO_2)_L}\right] \left[\frac{(Na)_L}{(Na)_R}\right]^2 \qquad (5)$$

it follows that

$$\frac{R-1}{(SO_4)} = Q_1 + Q_1Q_2(SO_4) + \ldots \qquad (6)$$

If only the first complex, UO_2SO_4, is formed, the quantity on the left of Equation 6 will be constant (simply Q_1) at constant ionic strength; variation of this quantity with changes in concentration of sulfate, however, will imply the formation of higher complexes. In the measurements to date Q_1 is the only equilibrium quotient that need be considered because the measurements have been made at low concentrations of sulfate.

The equilibrium activity constant K is related to Q by the following equation; the activity coefficient for the complex UO_2SO_4 is assumed to be unity:

$$K = \frac{Q}{\gamma_{UO_2}\gamma_{SO_4}} \qquad (7)$$

Activity coefficients for (UO_2) and (SO_4) can be estimated from the Debye-Hückel equation

$$-\log \gamma_i = \frac{Z_i^2 A\sqrt{\mu}}{1 + \mathring{a}B\sqrt{\mu}} \qquad (8)$$

where A and B are known constants at given temperature$^{(1)}$ and å is the adjustable "distance" or "ion size" parameter.

The results of membrane equilibrium measurements between mixtures of sodium bisulfate — sulfuric acid and mixtures of sodium perchlorate — perchloric acid are summarized in the following table. In these measurements the ratios of acid to salt were varied, but the total concentration of perchlorate ion and that of sulfate (SO_4^{2-} + HSO_4^-) ions were each constant. The variation in concentration of uncomplexed sulfate (SO_4^{2-}) is caused by the variation in acidity.

Values of K were calculated from the values of Q with Equations 7 and 8, with a value of å = 5 for the size parameter in Equation 8; this value for å yielded the best agreement between the membrane equilibrium results at $\mu = 0.1$ to 0.2 and potentiometric results$^{(2)}$ published for $\mu = 1$. The only membrane measurement that seems to be anomalous is

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(1) Robinson, R. A. and R. H. Stokes. Electrolyte Solutions. p. 491, Butterworths, London (1955).

(2) Ahrland, S. Acta. Chem. Scand. 6, 1151 (1951).

that for the highest ionic strength, $\mu = 0.2$, which was omitted from the average value; formation of the second complex may be significant at this higher ionic strength.

Formation Constants for UO_2SO_4
in Mixtures of H_2SO_4 and $NaHSO_4$ at 25°C
Membrane Equilibrium

μ	$(Na)_R/(Na)_L$	$(UO_2)_R/(UO_2)_L$	(SO_4)	$Q = \frac{R-1}{(SO_4)}$	K
0.149	1.215	9.064	0.0272	189	1730
0.156	1.267	10.31	0.0307	177	1680
0.166	1.318	12.67	0.0354	178	1750
0.172	1.356	14.34	0.0395	172	1740
0.189	1.442	17.36	0.0477	154	1700
				avg	1720
0.207	1.534	24.49	0.0564	167	2000

Measurements at widely differing values of ionic strength and temperatures are summarized in the following table. The measurements were made with $HClO_4$ (but without $NaClO_4$) on one side of the membrane and with H_2SO_4 (without $NaHSO_4$) on the other side. The published potentiometric result for $\mu = 1$ is included. The measurements at 25°C were extended to very low ionic strength; the results for the two most dilute systems have quite limited reliability because of experimental difficulties. The values for K were calculated from values for Q in the manner described for the data in the preceding table.

Formation Constants for UO_2SO_4
Membrane Equilibrium

	μ	Q	K	K_{Avg}
25°C				
	1.00(a)	50(a)	1740	
	0.149	189	1730	1700
	0.084	294	1850	
	0.046	342	1520	
	0.022	525	1490	
	0.010	650	1400	
35°C				
	0.156	254	2500	2330
	0.086	331	2150	
50°C				
	0.152	350	3580	3510
	0.0784	525	3440	

(a) Published data, Reference 2

The logarithms of the three experimental values for K are plotted against 1/T in Figure 25. The slope of (-1.20 ±.01) x 10^3 corresponds to an enthalpy of formation for the reaction, ΔH = +5.48 kcal/mol.

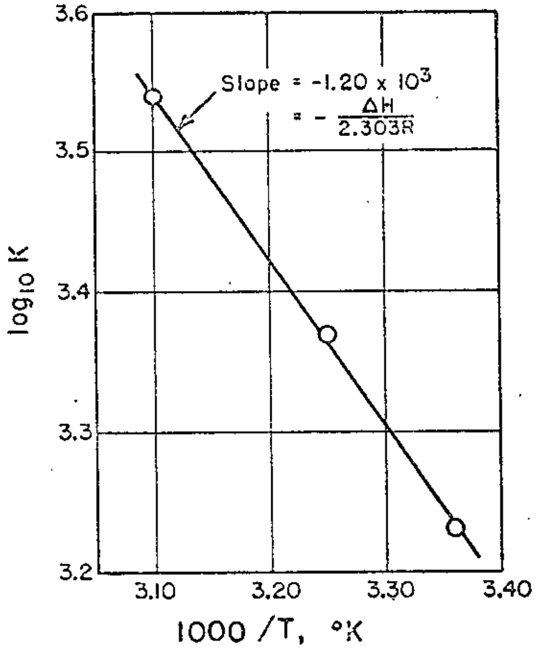

FIG. 25 TEMPERATURE DEPENDENCE OF K
$UO_2^{2+} + SO_4^{2-} = UO_2SO_4$

Experiments are in progress to increase the reliability of measurements at low ionic strength so that the value of the size parameter å can be defined more accurately for improved calculations of K. The measurements will be extended to higher concentrations of sulfate to determine the effects of formation of the second sulfate complex $[UO_2(SO_4)_2]^{2-}$.

MEMBRANE EQUILIBRIUM STUDIES

Study of the equilibrium constant for formation of the uranyl sulfate complex

$$UO_2^{2+} + SO_4^{2-} = UO_2SO_4 \qquad (1)$$

by measuring equilibrium conditions across ion exchange membranes was continued. The methods described in the February report were extended to measurements with solutions of lower ionic strength. This was done to obtain an estimate of the ion size parameter, $\mathring{a}$, in the Debyl-Huckel equation so that the equilibrium quotients could be extrapolated more reliably to infinite dilution.

The value $\mathring{a} = 8.22$ Å provides the best fit of the Debye-Huckel equation to the new data. With this value for $\mathring{a}$, average values of K were calculated to be 1510 at 25°C, 2080 at 35°C, and 2860 at 50°C. These values are slightly lower than those that were calculated with $\mathring{a} = 5$ Å and summarized in the February report. The value of the enthalpy change, ΔH, for Reaction 1 was calculated to be +4.88 kcal/mol on the basis of the new values for K; the value calculated in February was +5.48 kcal/mol.

The techniques used with the more dilute solutions were essentially the same as those described in the February report, with two basic modifications to improve accuracy and sensitivity:

1. The tracer concentrations of U^{233} and Na^{22} were absorbed by the membrane before the equilibrations were made. Equilibrium was attained in 5 to 6 hours rather than the 20 hours required previously, and the amounts of water and sulfate transported during equilibration were reduced significantly. Thus, the solutions on opposite sides of the membrane were kept more easily at constant ionic strength, a condition that is required for accurate calculation of the equilibrium constants. Reduction of the sulfate transport to a negligible amount removed the necessity for making corrections.

2. The tracer concentration of U^{233} was increased by a factor of 5. This increase permitted reliable values of Q, the equilibrium quotient in terms of concentration, to be obtained at ionic strength as low as 0.01. Attempts to determine the quotient at even lower concentrations were not successful because of inadequate uranium in the aqueous phases.

The values of the equilibrium constants determined at various values of ionic strengths at 25, 35, and 50°C are shown in the following table. The successive columns show the ionic strength, μ; the equilibrium quotient in terms of concentrations, Q; and the equilibrium constants in terms of activity, K, which are calculated from Q by means of the Debye-Huckel equation with $\mathring{a} = 8.22$ Å.

Formation Constants for UO_2SO_4
Membrane Equilibrium

	μ	Q	K	k_{avg}
25°C				
	0.0123	710	1580	1510
	.0220	540	1450	
	.0224	535	1450	
	.0394	447	1500	
	.0382	455	1510	
	.0809	330	1490	
	.1397	275	1570	
35°C				
	0.0113	956	2100	2080
	.0120	916	2060	
	.0205	695	1860	
	.0206	817	2190	
	.0358	629	2080	
	.0363	585	1940	
	.0732	499	2210	
	.1336	379	2160	
50°C				
	0.0107	1242	2630	2860
	.0181	1166	3090	
	.0311	935	3010	
	.0675	692	3080	
	.1260	427	2510	

Calculations of Q from the distribution of U^{233} and Na^{22} were made in the manner described in the February report. The ion size parameter was calculated by iteration on the basis of the following relationships.

$$\log Q = \log K + \log \gamma_{UO_2}\gamma_{SO_4} \qquad (2)$$

$$\log \gamma_{UO_2}\gamma_{SO_4} = \frac{-\,8A\sqrt{\mu}}{1 + \mathring{a}B\sqrt{\mu}} \qquad (3)$$

$$a = \mathring{a}_o + \delta \qquad (4)$$

where

$\mathring{a}_o$ = arbitrary value assumed for $\mathring{a}$

δ = correction term, assumed to be small

If Equations 2, 3, and 4 are combined, the following is a first order approximation to the resulting equation:

$$\log Q + \frac{8A\sqrt{\mu}}{1 + \mathring{a}_o B\sqrt{\mu}} = \log K + \frac{B}{8A}\,\delta\left(\frac{8A\sqrt{\mu}}{1 + \mathring{a}_o B\sqrt{\mu}}\right)^2 \qquad (5)$$

A graph of Equation 5 yields a slope from which δ can be calculated. A better approximation to $\mathring{a}$ can then be obtained from Equation 4 and the process can be repeated until δ becomes zero. With the present data and an initial choice of $\mathring{a}_o = 5$, only two iterations were required.

A new value for the enthalpy change, ΔH, of Reaction 1 was calculated from the average values of K at 25, 35, and 50°C from a plot of log K vs $\frac{1}{T}$. The new value is +4.88 compared with +5.48 kcal/mol reported in February. The difference is due largely to the different value of $\mathring{a}$.

Experiments are in progress to measure the equilibrium constants at higher ionic strength (~1M) so as to define the limits of applicability of the membrane technique and to find evidence for the existence of $UO_2(SO_4)_2^{=}$. Plans have also been made to study the complexing between uranyl ion and other ligands such as oxalate and EDTA.

MEMBRANE EQUILIBRIUM STUDIES

Determinations of the equilibrium quotients for formation of uranyl sulfate complexes by measuring equilibrium conditions across ion exchange membranes were concluded. The methods described in the February and April reports were extended to solutions of higher ionic strength and lower acidity, in which the equilibrium quotients for both the first and second uranyl sulfate complexes could be measured:

$$UO_2^{2+} + SO_4^{2-} = UO_2SO_4 \qquad (1)$$

$$UO_2SO_4 + SO_4^{2-} = [UO_2(SO_4)_2]^{2-} \qquad (2)$$

The following equilibrium quotients in terms of concentration for the foregoing reactions were measured:

Temp, °C	Q_1	Q_2
25.0	135	654
34.2	182	1280
47.8	237	2480

The corresponding calculated enthalpies of reaction are:

$$\Delta H_1 = +4.58 \text{ kcal/mol}$$
$$\Delta H_2 = +11.0 \text{ kcal/mol}$$

The equilibrium quotients were determined by measuring the distribution of U^{233} and Na^{22} between a solution of 0.3M $NaClO_4$ on one side of the membrane and a mixed solution of $NaClO_4$ and Na_2SO_4 on the other side. The composition of the mixture was varied through several sulfate concentrations between 0.02 and 0.1M with the ionic strength maintained at 0.3 in all cases. A small concentration of acid (~0.001M $HClO_4$) was also added to each cell to prevent the hydrolysis of uranyl ion. The techniques of the measurements were described in the February and April reports, except that "Amfion"* C-103 cation membranes were used because they were found to be more permeable to cations and less permeable to anions than the membranes that were used in previous measurements.

The equilibrium quotients were calculated by the method described in the February report, in which the following equation was shown to be valid at constant ionic strength if two complexes are formed

$$\frac{R-1}{(SO_4)} = Q_1 + Q_2(SO_4) \qquad (3)$$

where $R = (U_R/U_L)(Na_L/Na_R)^2$

and the subscripts R and L designate, respectively, the side

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* "Amfion" is a trademark of American Machine & Foundry Co.

Effect of Channel Thickness on Attainment of Steady State

Measurements of the rate of approach to steady state were made with two channel thicknesses. The feed solution channels are 63 mils thick in both cases; the stripping solution channel is 63 mils thick in one case, 15 mils in the other. Each channel is 36 inches long and 0.5 inch wide. The apparatus contains five pairs of channels in series. The membranes are "AMFion"* C103-C; the total exposed area is 90 in^2.

All measurements were made with feed containing 0.01M $UO_2(NO_3)_2$ and with stripping solution containing 2M HNO_3. The feed flow was 6 ml/min; the strip flow, 0.090 ml/min. The feed streams were agitated with thirty 5-ml pulses per minute.

The concentrations of uranium in the product streams as functions of time are shown in Figure 18. The concentration increases more rapidly with the 15-mil stripping channel because of the reduced volume of the thin channel. After 22 hours the steady-state concentration was 0.347M with the thin channel and 0.280M with the thick channel.

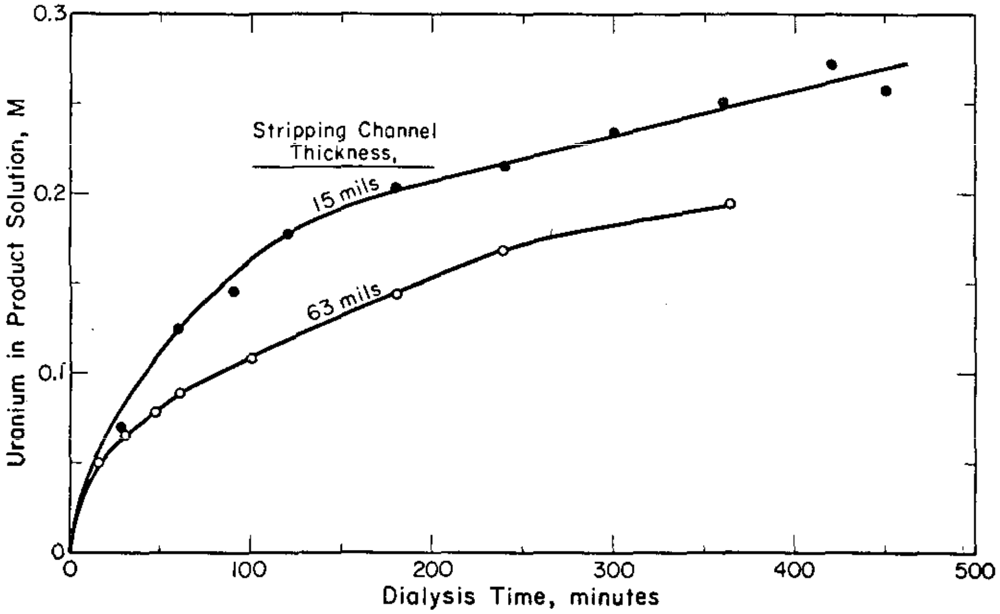

FIG. 18 CONCENTRATION OF UO_2^{2+} BY DIALYSIS

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* Trademark of the American Machine and Foundry Company.

Thick Channel Separator with Pulsing

Feed 0.01M $UO_2(NO_3)_2$

Flow (G_F), ml/(min)(100 cm^2)			Uranium Content		
			Raffinate (P_R), % of feed		Product,
Feed	Product	α	Observed	Calculated	M
Stripping solution 2M HNO_3					
0.689	0.0239	1.5	1.08	2.20	0.253
	.0296	1.88	0.67	0.58	.229
	.0302	2.00	0.54	0.46	.220
0.862	0.0258	1.5	2.72	4.05	0.317
	.0295	1.64	2.35	2.56	.283
	.0353	2.0	1.25	1.32	.259
	.0455	3.0	0.75	0.74	.191
	.0582	4.0	0.50	0.66	.149
1.38	0.0358	1.50	11.9	11.8	0.345
	.0441	2.0	8.47	6.75	.290
	.0643	3.0	4.65	5.05	.205
1.72	0.0396	1.45	22.3	19.0	0.349
	.0544	2.00	14.9	11.8	.288
	.0710	1.90	11.5	12.4	.222
Stripping solution 3M HNO_3					
0.862	0.0142	1.50	4.01	4.05	0.372
	.0283	1.80	1.70	1.79	.291
	.0308	2.00	1.28	1.32	.282
	.0360	2.75	0.75	0.80	.211
	.0434	3.00	0.56	0.74	.200
	.0532	4.2	0.57	0.64	.162
1.033	0.0255	1.50	7.00	6.20	0.399
	.0277	1.63	4.30	4.53	.323
	.0350	2.00	2.22	2.68	.276
	.0426	2.93	1.80	1.75	.233
	.0462	3.00	1.45	1.72	.219
	.0486	3.43	1.62	1.62	.210
	.0517	4.00	1.45	1.55	.200
1.38	0.0308	1.50	11.8	11.8	0.402
	.0358	1.82	8.63	7.85	.342
	.0391	2.00	7.33	6.73	.331
	.0458	2.80	6.61	5.27	.283
	.0474	3.00	6.34	5.12	.273
	.0596	3.30	4.74	4.95	.224
	.0662	4.00	4.43	4.75	.200

Effect of Other Operating Conditions on the Concentration of Uranium

Tests were made of the effects, on uranium concentration and yield, of (1) the concentration of acid in the stripping solution, (2) the flow rate of the feed, and (3) the parameter

$$\alpha = \frac{C_o g_o}{2U_F g_F}$$

where C_o, g_o = HNO_3 concentration and flow of stripping solution

U_F, g_F = $UO_2(NO_3)_2$ concentration and flow of feed solution

The tests were made with 63-mil feed channels and 15-mil strip channels; the total membrane area was 90 in^2. The feed flow was agitated with thirty 5-ml pulses per minute. The feed contained 0.01M $UO_2(NO_3)_2$; the stripping solution, either 2 or 3M HNO_3. All tests were continued to steady state.

The results, shown in the table on page 56, are similar to those obtained previously (June 1965 report, p 52). Both the concentration of uranium in the product stream and the loss to the raffinate increase with decreasing α and increasing feed flow. (The product concentrations were higher and the raffinate losses were lower than in the 1965 tests.) Also, for the same α and feed flow the uranium product was more concentrated when 3M HNO_3 was used in the stripping solution, but the loss to the raffinate was virtually independent of the acid in the strip.

At constant feed flow, an increase in α decreased the loss of uranium to the raffinate, to a constant value that depended on the feed flow. The loss of uranium to the raffinate, P_R, is represented by the empirically derived equation

$$\ln P_R = 4.92 - \frac{4.71}{G_F} + \frac{5.23}{G_F^{3/2}\alpha^3} \qquad (1)$$

where G_F = flow, ml/(min)(100 cm^2 membrane)

The calculated values of P_R in the preceding table were obtained with this equation. The feed flow in this equation and in the table are normalized to unit area of membrane.

Concentration Without Pulsing

The indication from previous work that pulsing of the feed flow is necessary implies that the rate-determining step in membrane separators is ion diffusion to the membrane surface rather than through the membrane. Agitation might therefore be eliminated if the diffusion rate within the feed solution could be increased.

Diffusion within a channel is visualized best with an idealized model, with channel length L, width W, and thickness ℓ. One side of the channel is impervious to solute and the other side -- the membrane -- is so permeable that the concentration of solute at the surface is zero. Feed solution enters the flow channel with uniform concentration C_o. As it moves along the membrane, a concentration gradient develops across the channel. If the flow is independent of the distance from the walls and no diffusion occurs in the direction of flow, then the distribution of solute within the channel at any distance y is the same as in a static solution after the time t that is required for the flowing solution to reach y. For the large values of the parameter Dt/ℓ^2 for membrane separators, the average concentration $\overline{C}$ in the channel is(1)

$$\overline{C} = C_o \frac{8}{\pi^2} e^{-\frac{\pi^2}{4}\frac{Dt}{\ell^2}} \qquad (2)$$

where D = diffusion coefficient, cm^2/sec

The time required for the solution to traverse the length L of the channel is

$$t = L/v \qquad (3)$$

and the linear velocity v (cm/min) is related to the volumetric velocity g (ml/min) by

$$g = \ell W v \qquad (4)$$

By combination of Equations 2, 3, and 4

$$\frac{\overline{C}}{C_o} = \frac{8}{\pi^2} e^{-\frac{\pi^2}{4}\frac{DA}{\ell g}} \qquad (5)$$

where A = total membrane area (LW)

$\overline{C}/C_o$ = fractional loss to raffinate

The only unknown quantity is the diffusion coefficient, D.

Three tests were made to determine the validity of Equation 5. A solution of 0.01M $UO_2(NO_3)_2$ was fed into the 63-mil channel (1.6 mm) at various flows, and the 3M HNO_3 stripping solution was fed at flows sufficiently high to give large values of α. These conditions approached those required by the model -- to provide the largest possible exchange of UO_2^{2+} through the membrane. The streams were not pulsed.

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(1) H. S. Carslaw and J. C. Jaeger. Conduction of Heat in Solids. 2nd Ed., p 97.

The results of these tests are shown in the following table. In Figure 19, the losses to the raffinate are compared with pulsed tests at large values of α.

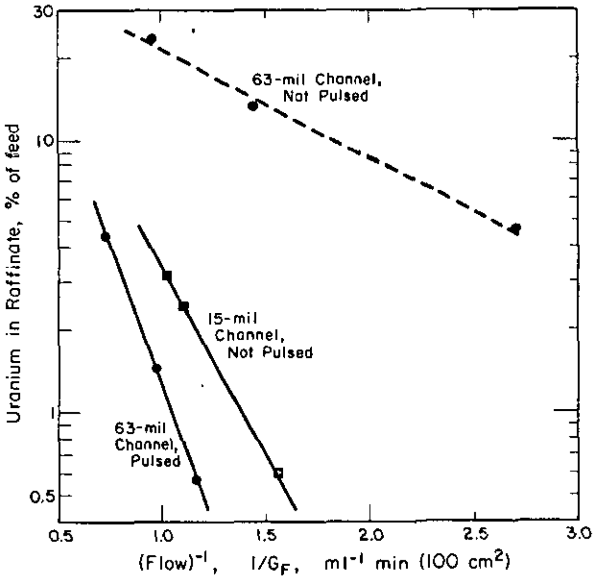

FIG. 19 EFFECTS OF PULSING AND CHANNEL THICKNESS

Diffusion coefficients were calculated with Equation 5 from the results of these tests and are given in the table. These coefficients agree reasonably well with published values for most salts in aqueous solutions, (1 to 2) x 10^{-5} cm^2/sec at 25°C. Thus, the rate-determining step is indeed diffusion within the feed channel, and Equation 5 adequately describes the diffusion.

Thick Channel Separator Without Pulsing

Feed 0.01M $UO_2(NO_3)_2$ Strip 3M HNO_3

Flow (G_F), ml/(min)(100 cm^2) Feed	Product	α	Uranium Content Raffinate, % of feed	Product, M	Diffusion Coefficient, 10^{-5} cm^2/sec
0.345	0.0281	3.75	4.65	0.123	1.07
0.689	0.0383	3.59	13.5	0.160	1.35
1.033	0.0479	2.85	23.6	0.171	1.39

If a membrane separator is operated efficiently without agitation, the quantity $\overline{C}/C_o$ in Equation 5 must approach that obtained with agitation. This result can be obtained conveniently by decreasing ℓ. Increasing the A/g ratio would also reduce $\overline{C}/C_o$, but would have the same effect on the agitated separation as well.

Furthermore, an increase in A/g would increase the residence time per unit area of membrane, which causes dilution of the product by osmosis. Calculation (Equation 5) with the foregoing experimental values for the diffusion coefficient shows that values of $\overline{C}/C_0$ for the pulsed and nonpulsed systems become similar when $\ell \approx 0.4$ mm (~15 mils).

Initial attempts to use very thin channels were unsatisfactory because the membrane distorted and blocked the channels. Blockage was prevented by supporting the membrane on screens. One membrane and two channels were used. The channels were formed by cutting 1- by 36-inch slots in a 15-mil polyethylene sheet, and contained 12-mil stainless steel screen.

The results of tests without pulsing, in which α and the flow of the uranium stream were varied, are given in the following table and also (for those with large values of α) in Figure 19. The losses to the raffinate in these tests were much lower than those in the 63-mil channels without pulsing, when normalized to the same flow per unit area of membrane. Losses were slightly higher than those with the pulsed system because ~20% of the membrane was masked by the screen. The losses to the raffinate are represented quite well by Equation 1, if only 80% of the membrane is accessible. The raffinate losses in the table were so calculated.

These tests demonstrate that uranium can be concentrated adequately, with sufficiently low loss, to enable the design of practical apparatus without pulsing. The pressure drop across the apparatus under normal operating flows was only 25 to 30 cm of H_2O, so that pumping requirements are expected to be nominal.

Thin Channel Separator Without Pulsing

Feed 0.01M $UO_2(NO_3)_2$ Strip 3M HNO_3

Flow (G_F), ml/(min)(100 cm²)			Uranium Content		
			Raffinate, % of feed		Product,
Feed	Product	α	Observed	Calc	M
0.642	0.0473	4.6	0.60	0.44	0.145
0.909	0.0448	3.3	2.46	2.44	0.201
0.969	0.0457	3.05	3.20	3.22	0.212
0.672(a)	0.0357	2.6	0.74	0.73	0.196
0.655(b)	0.0353	2.7	0.64	0.65	0.197
0.861	0.0342	2.0	2.34	3.60	0.247
0.991	0.0338	1.75	3.86	6.40	0.289

(a) 7-hour test
(b) 24-hour test

Further tests of the thin-channel separators, with five times the present membrane area, are underway in the continuing program to design and fabricate a practical separator.

Tubular Membrane Separators

Because a bundle of small tubes of ion exchange membrane in a shell assembly is conceptually the most convenient way to provide countercurrent flows in contact with large membrane surface in a compact device, arrangements were made for development of tubular cation exchange membrane by the Polymer Research Division of the Illinois Institute of Technology Research Institute (IITRI).

In the first successful fabrication, IITRI extruded and sulfonated a mixture of polyethylene and polystyrene to produce tubing with ~50-mil diameter and 4-mil wall. Mass transport tests were made in the laboratory with a 4-ft length of this tubing at the axis of a 15-mm glass tube. The osmotic flux and nitric acid flux were measured with nitric acid flowing through the membrane tubing while water flowed countercurrently through the shell. The flux of nitric acid is a measure of the anion leakage of the cation exchange membrane. The uranium exchange flux was then measured with 0.06M uranyl nitrate solution flowing through the shell. The properties of the membrane tubing are compared with those of "AMFion" C103-C in the following table; the flux parameters are defined as follows:

1. K_w, the osmotic flux parameter, is a measure of the flow of water through a membrane from pure water into a nitric acid solution:

$$K_w = \Phi_w / A\bar{C}$$

where Φ_w = flux of water, grams/minute
A = area of membrane, cm^2
$\bar{C}$ = average concentration of nitric acid, M

K_w was determined to be constant over the range of acid concentrations studied (~2-3M).

2. K_a, the nitric acid flux parameter, is a measure of the leakage of nitric acid through the membrane into water (in the same test used for measuring K_w):

$$K_a = \Phi_a / A\bar{C}$$

where Φ_a = flux of nitric acid, millimoles/minute

3. K_u, the uranium flux parameter, is a measure of the maximum exchange flux of uranyl and hydrogen ions through the membrane:

$$K_u = (\Phi_u)_{max}/A$$

where $(\Phi_u)_{max}$ = flux of uranium, millimoles/minute, across the membrane when one surface is essentially saturated with uranyl ion and the other with hydrogen ion

Comparison of Cation Exchange Membranes

	IITRI Tubing	"AMFion" C103-C Sheet
Osmotic flux, K_w g cm min^{-1} millimole^{-1}	3.9×10^{-4}	3.0×10^{-4}
HNO_3 flux, K_a cm min^{-1}	4.3×10^{-4}	1.2×10^{-4}
Uranium flux, K_u millimole min^{-1} cm^{-2}	4.3×10^{-4}	2.5×10^{-4}
Capacity, meq/g	2.17 ±0.2	1.2 ±0.2[(a)]
Water in H^+ form, %	60	15 ±3[(a)]

(a) Specifications of American Machine and Foundry

The five tabulated properties are related in concentrating uranyl ion or other cations by Donnan dialysis. High cation exchange capacity increases the transfer of cations and reduces that of anions. The water content is a measure of swelling, which affects the transport of both cations and anions. A decrease in swelling decreases both the cation and anion fluxes -- the anion effect is much larger. The high water content of the tubular membrane is consistent with its high osmotic flux.

The tubular membrane has excellent capacity and uranium exchange flux, and its osmotic flux is acceptable, but the water content and nitric acid flux (anion leakage) are higher than desired.

To increase the usefulness of tubular membranes, a new batch will be made by IITRI in which the two polymers are crosslinked by exposure to gamma radiation. Crosslinking is expected to tie the structure more tightly and thereby reduce the nitric acid flux and water content, and improve the physical strength.

ION EXCHANGE MEMBRANE SEPARATIONS

In continued development of ion exchange membrane dialysis for concentrating or separating ions in solution, the effects of design parameters on the expected performance of flat-membrane equipment were defined. Ion exchange dialysis has been demonstrated at laboratory scale to be potentially useful. The most immediate use foreseen in the plant is to concentrate uranyl ions of ^{235}U or ^{233}U in solvent extraction products to solutions suitable for conversion to uranium oxide or metal. Membrane dialysis has the principal potential advantages of continuous operation and ease of replacement of the exchanger.

Adaption to plant use depends upon the development of compact equipment that will operate reliably and in which the membranes can be replaced easily. Two types of such equipment are being studied; one with flat commercial membranes, the other with tubular membranes not yet available commercially. This section describes the present development of flat-membrane equipment.

In most of the earlier tests, uranium was concentrated in flat-membrane assemblies containing relatively thick channels (~63 mils) in which the flows were pulsed to provide agitation. Results in the March report (p 54) indicated that pulsing is not needed if the channels are sufficiently thin (~15 mils). Because of dimensional differences these preliminary tests were with apparatus containing only one pair of 3-ft channels, and could not be compared reliably with the tests in the thick-channel apparatus. The present experience with apparatus containing five 3-ft pairs of thin channels has shown that:

> Loss of uranium to the raffinate is lower with the thin-channel assembly without pulsing than with the thick-channel apparatus with pulsing. The product concentrations were about the same in both systems.
>
> Loss is slightly higher with shorter channels.
>
> Uniform flow in the five channels is difficult to maintain when five channels are in parallel and fed through manifolds; loss of uranium to the raffinate is higher than in series channels.
>
> The thin-channel separator can concentrate uranium from 1 to 60 g/l with adequately low loss to raffinate.
>
> The thin-channel separator is compatible with the recycle process described in the October 1965 report (p 83).

Concentration of Uranyl Ion in Thin-Channel Separator

A thin-channel separator was constructed in the test assembly described in the September 1966 report (p 86). Each channel is a 1- by 36-inch slot in a 15-mil polyethylene sheet, fitted with a 12-mil stainless steel screen. The feed and stripping channels are separated by "AMFion"* C103-C cation membranes and clamped in the apparatus, which contains five such pairs of channels with all feed and strip channels connected in series by external connections to provide a single effective pair of 15-ft-long channels. When shorter overall length is desired, the appropriate individual channels are disconnected. When parallel flow is desired, the external connections are changed to obtain independent pairs of channels that operate simultaneously.

Five Channels in Series

The concentration of 0.01M uranyl nitrate with 3M nitric acid strip was tested with the five channels in series, without pulsing. The feed flow and the parameter α were varied to give a direct comparison with pulsed-flow results (March report, p 56) with the thick-channel apparatus. The parameter

$$\alpha = C_o g_o / 2\ U_f g_f$$

where C_o, g_o = HNO_3 concentration and flow of stripping solution

U_f, g_f = $UO_2(NO_3)_3$ concentration and flow of feed solution

The results are compared in the following table. Losses to the raffinate were much lower with the thin channels. The uranium concentrations of the product streams are very nearly the same in both systems.

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* Trademark of the American Machine and Foundry Co.

Concentration of Uranium in Thin-Channel Membrane Separator

Feed 0.01M $UO_2(NO_3)_2$ Strip 3M HNO_3

Flow, ml/(min)(100 cm^2)			Uranium Content			
			Raffinate, % of feed		Product, M	
Feed	Product	α	(A)	(B)	(A)	(B)
0.690	0.0283	1.56	0.023		0.225	
0.862	0.0256	1.50	0.83	4.05	0.335	0.372
	0.0344	2.00	0.10	1.28	0.257	0.282
	0.0480	3.00	0.07	0.56	0.182	0.200
1.034	0.0276	1.50	2.19	7.00	0.381	0.399
	0.0362	2.00	0.58	2.22	0.298	0.276
	0.0427	3.50	0.23	1.45	0.191	0.210
1.207	0.0284	1.50	4.39		0.415	
	0.0415	2.00	0.99		0.301	
1.379	0.0315	1.50	5.23	11.8	0.421	0.402
	0.0415	2.00	2.00	6.73	0.325	0.331
	0.0575	3.00	1.04	5.12	0.241	0.273
1.552	0.0366	1.50	5.77		0.404	
	0.0463	2.00	2.83		0.324	

(A) Thin channels - no pulsing
(B) Thick channels - with pulsing

Effect of Channel Length

The operation of a membrane separator has been assumed to be describable in terms of the feed flow per unit area, independent of the length and width of the channels. Because of end effects, this assumption is an oversimplification in real separators. In addition, the pressure drop and linear flow may affect such systems. The effect of channel length was determined in two series of tests in which the length was varied and the feed flow per unit area of membrane was the same. Two different values of α were used in each series.

The results of these tests are shown in the following table. With channel lengths of ⩾9 ft, the product concentrations and losses to the raffinate are not particularly sensitive to channel length. A 6-ft channel, however, gave significantly larger losses to the raffinate, particularly at low flow.

Effect of Channel Length on Efficiency of a Membrane Concentrator

Channel width 1 inch Feed 0.01M $UO_2(NO_3)_2$ Strip 3.0M HNO_3

Channel Length, ft	Feed Flow, ml/(min)(100 cm²)	α	Uranium Content Raffinate, % of feed	Uranium Content Product, M
15	1.55	1.5	5.77	0.404
12	1.55	1.5	7.17	0.439
9	1.55	1.5	6.98	0.394
6	1.55	1.5	9.03	0.410
15	1.55	2.0	2.83	0.324
12	1.55	2.0	3.04	0.328
9	1.55	2.0	4.13	0.341
6	1.55	2.0	5.80	0.329
15	1.03	1.5	2.19	0.381
12	1.03	1.5	1.37	0.347
9	1.03	1.5	1.60	0.336
6	1.03	1.5	4.75	0.390
15	1.03	2.0	0.58	0.298
12	1.03	2.0	0.54	0.282
9	1.03	2.0	0.70	0.268
6	1.03	2.0	2.06	0.298

Parallel Flow Effects

The most convenient type of membrane separator would use countercurrent flow of the feed and stripping streams through parallel- rather than series-connected channels. The pressure drop in the parallel channels is much smaller, each channel except at the end plates is bounded by two membranes, and the flow of the two streams is completely countercurrent.

Exact construction of such a parallel system in the present test assembly was not possible; however the five pairs of channels were connected in parallel and fed through manifolds. Initial tests showed that the flow through the channels was not uniform, especially in the strip channels where the pressure drop is very small (~1 cm of H_2O); at times, a few of these channels carried all of the flow.

A device was constructed to divide the pumped strip solution into five streams of equal flow that were then fed by gravity into the five separate strip channels. The feed stream was introduced through a manifold, as before. This device allowed the parallel-channel system to be tested. The following table compares losses to the raffinate from the parallel system with data from similar tests (p 74) in which the same five pairs of channels were connected in series. Although the losses are considerably higher in the parallel system, this system should still operate adequately in a recycle process. Whether the higher losses in the parallel system are due to nonuniform flow through the feed channels, or due to the short (3 ft) feed channels, is not yet certain. The latter seems more probable because the operation of this system is in accord with the trend established in the foregoing section.

Although uniform flow through the strip channels was provided by the feed device, the pressure drop across the several channels varied considerably -- 0.5 to 1.5 cm of H_2O. This indicates that extreme care is needed in designing these channels if a manifold is used.

Effect of Parallel Flow on Efficiency of a Membrane Concentrator

Feed 0.01M $UO_2(NO_3)_2$ Strip 3.0M HNO_3

Feed Flow, ml/(min)(100 cm^2)	α	Uranium Content: Raffinate, % of feed: Parallel	Uranium Content: Raffinate, % of feed: Series	Uranium Content: Product, M: Parallel
0.862	1.5	3.57	0.83	0.283
1.034		5.35	2.19	0.316
1.207		5.86	4.39	0.310
1.397		8.71	5.23	0.332
1.552		10.2	5.77	0.342
0.862	2.0	1.87	0.10	0.237
1.034		3.04	0.58	0.244
1.207		3.94	0.99	0.249
1.397		5.91	2.00	0.270
1.552		8.17	2.83	0.291

Concentration of More Dilute Uranyl Nitrate Solution

In plant processes the uranyl nitrate in the feed may be less than the 0.01M (~2.4 g/l) concentration used in previous tests. In addition, if recycle is used, virtually all of the uranium in the raffinate from the first separator will have to be concentrated to approximately the original feed concentration. The following tests showed that the thin-channel separator will satisfy these requirements.

The following table shows the results of two tests in which 0.005M uranyl nitrate (~1.2 g/l) solutions were concentrated to ~60 g/l in the thin-channel apparatus (five pairs of channels in series). Losses were acceptably low -- much smaller than with more concentrated feed. This improved efficiency is attributed to the lower anion concentration in the feed stream, which should provide a greater driving force for uranium transport.

Also shown in the table are the results of the extraction of uranium from a simulated raffinate from the first concentrator in a recycle system. The composition of the stream (0.001M) is approximately that expected in the raffinate from a first-stage concentrator in which the feed is 0.01M uranyl nitrate, and the loss 10%. The thin-channel apparatus concentrated this raffinate to more than five times the original feed concentration with a loss to the final raffinate of only 0.1% based on the concentration in the first raffinate. This is equivalent to an overall loss of only ~0.01%.

Concentration of More Dilute Uranyl Nitrate Solutions

Feed Composition	Flow, ml/(min)(100 cm^2)	α	Uranium Content Raffinate, % of feed	Uranium Content Product, M
0.005M UO_2^{2+} No HNO_3	1.55	1.5	0.34	0.265
		3.0	0.14	0.160
0.001M UO_2^{2+} 0.02M HNO_3	1.55	12	~0.1	0.0565

These results prove the superiority of the thin-channel separators both in ease of operation (no pulsing) and in efficiency. Future work will include design and fabrication of practical separator units and a demonstration of the thin-channel separator with anion exchange membranes for deacidifying solutions of uranyl nitrate.

ION EXCHANGE MEMBRANE SEPARATIONS

In continued development of ion exchange membrane dialysis for concentrating or separating ions in solution, uranyl nitrate solution was deacidified in a thin-channel, anion exchange membrane separator. Ion exchange dialysis has been demonstrated at laboratory scale to be potentially useful: continuous operation is possible, and the exchanger can be replaced easily.

The first plant application is expected to be the concentration of ^{235}U or ^{233}U solutions. Plant use depends on the development of compact equipment that will operate reliably and in which the membranes can be replaced easily. Two types of such equipment are being studied: one with flat commercial membranes, the other with tubular membranes not yet available commercially. This section describes additional development tests with flat-membrane equipment.

A complete process for concentrating uranyl nitrate from plant solutions by Donnan dialysis was described in the June 1965 report (p 52). The first step is deacidification: uranyl nitrate flows along one side of an anion exchange membrane and sodium hydroxide along the other. NO_3^- and OH^- exchange through the membrane, and the OH^- neutralizes the acid. Transport of the cations is much slower.

Deacidifying dilute solutions of uranyl nitrate in a continuous anion exchange membrane separator is feasible (October 1965 report, p 82). Recently, highly efficient thin-channel membrane separators were developed and demonstrated for concentrating uranyl nitrate (September 1967 report, p 73). This section summarizes the application of thin-channel separators to deacidification and reports the effect of various operating conditions. The tests show that:

Solutions of uranyl nitrate can be deacidified in a thin-channel membrane separator. The amount of acid removed can be increased by adjusting the sodium hydroxide concentration and flow and the feed flow.

The flux of NO_3^- and OH^- ions across the membrane can be represented approximately as a function of the product of the concentration and flow of the sodium hydroxide stream.

The sodium ion flux is much smaller than the nitrate-hydroxide flux and depends, to a first approximation, on the concentration of the sodium hydroxide stream.

Uranium losses through the membrane are very low.

Thin-Channel Anion Exchange Separator

Deacidification was studied in a 15-foot thin-channel separator (September report) containing 1160 cm^2 of "AMFion"* A104-B anion exchange membrane. Feed containing 0.01M uranyl nitrate and 0.3M nitric acid was fed into one channel of the separator at various flows, while sodium hydroxide solutions between 1.5M and 0.25M were pumped into the other channel. The deacidified uranyl nitrate solution was analyzed for nitric acid and sodium ion; the spent sodium hydroxide, for uranium.

Results are summarized in the following table. The nitrate-hydroxide flux through the membrane ($\Phi_{NO_3^-}$) was calculated from the following equation:

$$\Phi_{NO_3^-} = \frac{[(HNO_3)_i - (HNO_3)_f]\ g_f}{A}$$

where $(HNO_3)_i$ = initial concentration in feed solution, M
$(HNO_3)_f$ = final concentration in feed solution, M
g_f = feed flow, ml/min
A = membrane area, $decimeter^2$

The sodium ion flux (Φ_{Na^+}) was determined from the equation:

$$\Phi_{Na^+} = \frac{(Na^+)_f\ g_f}{A}$$

where $(Na^+)_f$ = concentration in deacidifier feed, moles/liter

Although $\Phi_{NO_3^-}$ fluctuated slightly when the feed flow was varied, the nitrate-hydroxide flux was affected primarily by the concentration and flow of the sodium hydroxide. $\Phi_{NO_3^-}$ is dependent upon the product of the sodium hydroxide concentration (NaOH) and its flow g_{NaOH} for the three highest concentrations, as shown in Figure 12; the correlation is less close with 0.25M NaOH. This correlation implies that the anion flux is determined only by the molar flow of sodium hydroxide. The independence of anion flux on the feed flow simplifies calculation of operating conditions for removing all of the acid and aids in optimizing conditions.

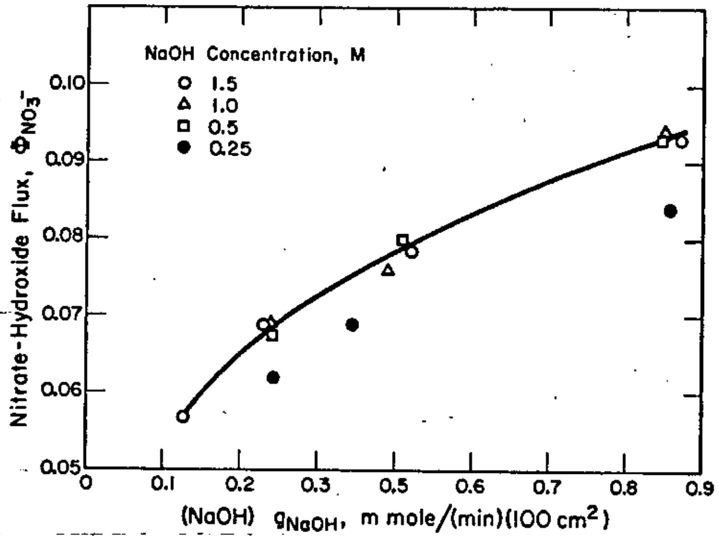

FIG. 12 ANION FLUX THROUGH MEMBRANES

The fractional neutralization of sodium hydroxide is:

$$F = \frac{\Phi_{NO_3^-}}{(NaOH)\ g_{NaOH}}$$

F varied from 0.1 to 0.25 as (NaOH) g_{NaOH} was decreased from 0.87 to 0.23. Membrane deacidifiers appear to be somewhat inefficient in utilizing sodium hydroxide when large anion fluxes are required.

The sodium ion flux Φ_{Na^+} appears to be dependent only on the concentration of sodium hydroxide. Although Φ_{Na^+} varies for the same sodium hydroxide concentration, no correlation with any other parameter is apparent; furthermore, the decrease in Φ_{Na^+} with decreasing concentration of sodium hydroxide is much greater than the variations at the same concentration -- as expected for ion exchange membranes. Thus, dilute sodium hydroxide will reduce the amount of sodium ion contaminating the uranium. Sodium ion concentrates to some extent with the uranium and may interfere with uranium precipitation in a later process.

Uranium losses to the spent sodium hydroxide were all less than 0.1%.

Thin-channel separators are being designed at plant scale; development of tubular membranes is also continuing.

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Deacidification of Uranyl Nitrate Solutions

Feed 0.01M $UO_2(NO_3)_2$ 0.3M HNO_3

Flow, ml/(min)(100 cm^2)		Deacidified Feed		Uranium in Spent NaOH, 10^{-6}M	Flux per (min)(100 cm^2)	
NaOH	Feed	$(HNO_3)_f$, M	$(Na^+)_f$, 10^{-3}M		$\Phi_{NO_3^-}$, mmole	Φ_{Na^+}, µmole
			1.5M NaOH			
0.58	0.520	0.1192	1.56	1.1	0.0953	0.811
	0.426	0.0831	1.93	1.2	0.0935	0.822
	0.325	0.0279	2.65	1.7	0.0893	0.861
0.35	0.522	0.1489	1.75	1.8	0.0802	0.914
	0.433	0.1151	2.20	1.9	0.0791	0.875
	0.259	0.0093	5.91	2.0	0.0759	1.53
0.22	0.345	0.1104	3.04	1.1	0.0663	1.05
	0.258	0.0230	4.61	1.5	0.0721	1.19
0.15	0.345	0.1370	3.26	1.4	0.0571	1.12
			1.0M NaOH			
0.85	0.527	0.1234	0.93	2.4	0.0944	0.490
	0.433	0.0872	1.04	1.9	0.0932	0.450
	0.329	0.0099	2.50	2.2	0.0963	0.822
0.48	0.463	0.1353	1.25	-	0.0774	0.579
	0.355	0.0877	1.53	1.4	0.0763	0.543
	0.254	0.0103	2.06	1.7	0.0742	0.523
0.34	0.346	0.1008	2.28	1.8	0.0697	0.789
	0.232	0.0130	3.30	1.8	0.0672	0.766
			0.5M NaOH			
1.69	0.516	0.1203	0.435	1.4	0.0942	0.224
	0.436	0.0880	0.426	0.9	0.0928	0.186
	0.317	0.0122	0.648	1.0	0.0922	0.205
1.03	0.520	0.1449	0.452	1.6	0.0820	0.235
	0.423	0.1149	0.469	0.9	0.0794	0.198
	0.326	0.0627	0.696	1.0	0.0782	0.227
0.68	0.343	0.1044	0.696	1.1	0.0682	0.232
	0.234	0.0220	0.965	0.9	0.0658	0.226
			0.25M NaOH			
3.45	0.439	0.1131	0.363	<1	0.0825	0.159
	0.286	0.0282	0.191	<1	0.0787	0.0552
	0.297	0.0040	0.356	1	0.0899	0.106
1.72	0.425	0.1368	0.356	1.2	0.0707	0.151
	0.339	0.0953	0.345	1.0	0.0704	0.117
	0.224	0.0052	0.332	1.2	0.0668	0.074
1.38	0.340	0.1307	0.343	1.6	0.0587	0.117
	0.212	-0.0044(a)	0.435	1.4	0.0652	0.0922

(a) Acid deficient

ION EXCHANGE MEMBRANE SEPARATIONS

In the development of ion exchange membrane dialysis for concentrating or separating ions in solution, improved designs and operating techniques were demonstrated to be adequate for constructing a thin-channel prototype plant separator containing flat membranes. Thin-channel (15-mil) separators are superior to thick-channel (60-mil) separators for concentrating uranium (September 1967 report, p 73). A plant-scale separator will require suitable thin-channel spacers and a satisfactory system for flow distribution.

The prospective separator will contain 100 to 200 membranes, separated by spacers and held together by end plates. The feed solution containing dilute uranyl nitrate enters at one end, flows uniformly through alternate channels in parallel, and emerges as the raffinate. The extractant containing nitric acid enters at the opposite end, flows counter to the feed through the alternate channels adjacent to the feed channels, and emerges as the product. The spacers must maintain uniform distribution of flow. A fabricated two-membrane, three-channel assembly is shown in Figure 17.

Construction of Spacers

The principal design problem is encountered in introducing the streams into the correct channel without crossflow between the two streams. In principle, crossflow can be prevented by a simple arrangement. A slot in each end of each spacer connects the ion exchange channel with the appropriate inlet or exit stream. In practice, the membranes must be bridged with a stiff material such as stainless steel to prevent them from bending into the slots and permitting the inlet streams to flow into adjacent "wrong way" channels.

A spacer to provide the bridging was constructed as a laminate of three layers of stainless steel shimstock, cemented with polyvinyl chloride (Figure 17). An alternative spacer that appears to be more resistant to nitric acid is made by thermal bonding of polyethylene to the ends of the stainless steel, membrane-supporting, screen in the channels.

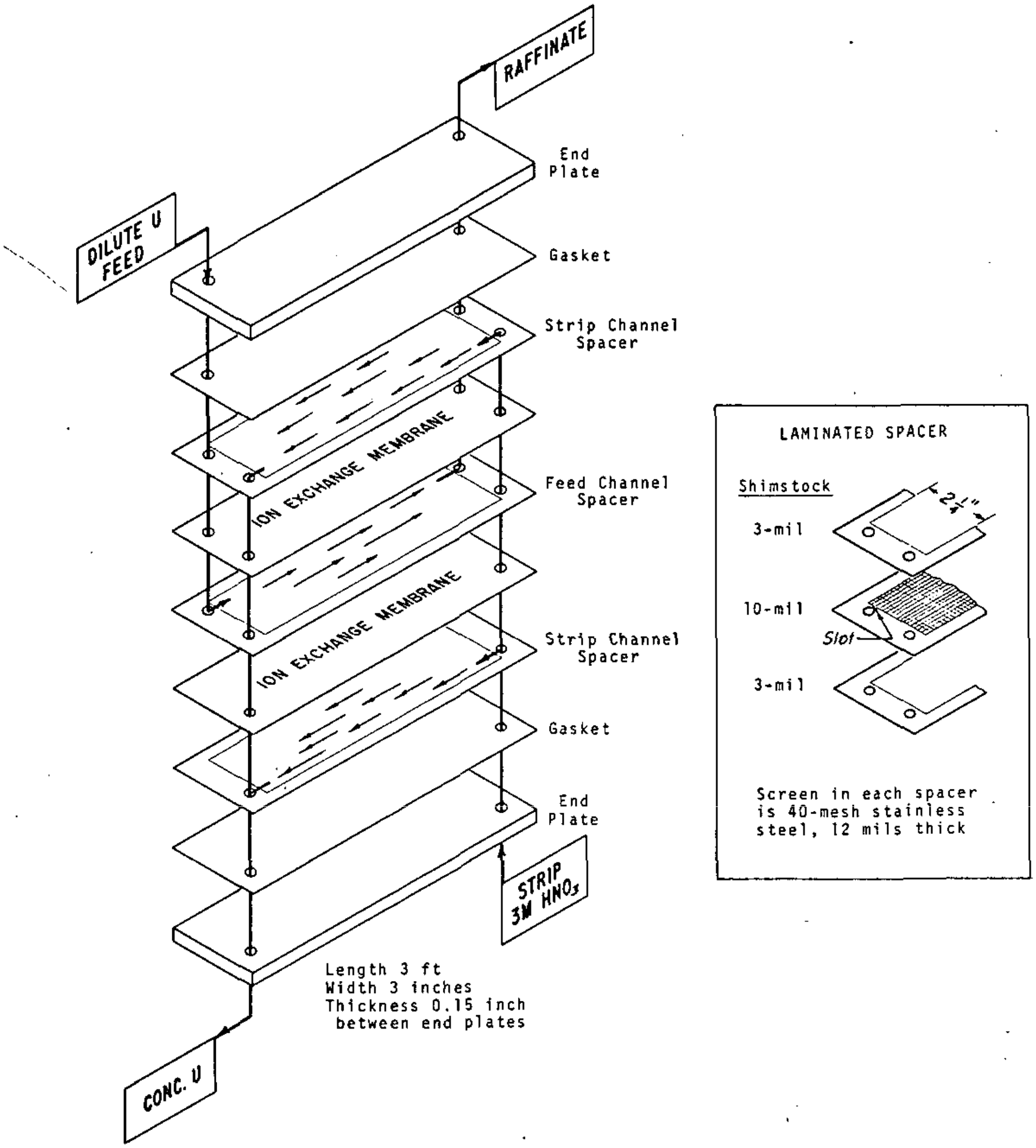

FIG. 17 TWO-MEMBRANE THREE-CHANNEL CONCENTRATOR

Tests of Thin-Channel Separator

The two-membrane, three-channel separator was tested by feeding 0.01M uranyl nitrate into the center channel and 3M nitric acid into the two outer channels. After the flows were started, the pressure in the outer channels was increased ~10 psi above that in the feed channel, to force the two membranes against the membrane-supporting screen in the feed channel and thereby reduce the rate-limiting diffusion distance in the feed channel to the minimum for this 12-mil-thick screen.

The effectiveness of this procedure was demonstrated in an experiment in which the flow of feed was 25 ml/min and the flow of nitric acid was 0.33 ml/min. When steady state was reached, the excess pressure in the outside channels was removed and a new steady state was reached. Removal of the pressure increased the uranium in the raffinate from 4.5 to 23.5%, and decreased the concentration of uranium in the product from 0.319 to 0.245M.

Tests at various flows are summarized in the following table. The feed flow was 75 times the flow of strip solution in each test.

The uranium "loss" in the raffinate is independent of feed flow at small flow, and increases gradually with larger flow. The loss is higher at low flow than was experienced with the simple two-channel apparatus (September 1967 report), but was lower at high flow. The relatively high loss at low flow and its independence of flow are attributed to a passage of a small fraction of each channel flow along the edges between the top and bottom shims without contact with the membrane. This can be corrected by spacer design. The lower loss at high flow is attributed to the pressurization, which makes the diffusion distance very small in the feed channel. The thickness of the feed channel is thus decreased to 12 mils (the thickness of the screen); the diffusion distance is $\leqslant 6$ mils to the nearest membrane.

These tests indicate that the capacity of a similar plant separator will exceed 3 ml/(min)(100 cm^2) if a "recycle" process is used (June 1965 report, p 52). The largest flow in the simple two-membrane device was 1.55 ml/(min)(100 cm^2).

In a further test of the recycle process in the thin-channel separator, a large batch of feed was processed at 3.63 ml/(min) (100 cm^2). The raffinate was reprocessed through the same device at the same flow, but at a sufficiently slow flow of nitric acid to concentrate the residual uranium to the original feed concentration. The product stream contained 0.34M uranium, only 0.04% of the uranium was in the final raffinate, and recycled raffinate contained 0.02M uranium. Because this test demonstrates that the separator can operate at twice the earlier flows, only half as many membranes are needed as under the conditions described in the September 1967 report.

Alternative spacer designs are being evaluated that may be easier and less expensive to fabricate. A five-membrane separator based on the best of these designs will be built for additional tests in the laboratory, preparatory to a plant prototype.

Concentration of Uranium in Thin-Channel Dialyzer

Feed 0.01M $UO_2(NO_3)_2$ Strip 3M HNO_3.
Feed/strip flow ratio 75

Feed Flow, ml/(min)(100 cm^2)	Uranium Content Raffinate, % of feed	Product, M
0.97	1.38	0.218
1.21	1.63	0.236
1.45	1.90	0.246
1.69	1.98	0.247
2.43	3.10	0.262
3.03	4.50	0.319
3.63	6.41	0.344
4.84	15.6	0.376

STABILITY CONSTANTS OF LANTHANIDE AND ACTINIDE COMPLEXES

Techniques were developed to determine stability constants of lanthanide complexes by two new methods: Donnan equilibrium across ion exchange membranes (page 51) and proton magnetic resonance (page 54).

Membrane Ion Exchange Equilibrium

The technique developed for determining stability constants of uranyl sulfate complexes by Donnan equilibrium across ion exchange membranes$^{(1)}$ was extended to determine the stability of chelates of trivalent lanthanides. Equilibrium concentrations are measured for reactions of the form

$$Ln_a^{3+} + Ln_bY^- \rightleftharpoons Ln_b^{3+} + Ln_aY^- \qquad (1)$$

where Ln_a, Ln_b = different lanthanides

Y = chelating anion

A sufficient number of sets of such concentrations are measured to permit the calculation of a series of relative stability constants for the various lanthanides or anions, which are then normalized to an accurately known constant in the series. This approach is similar to a published analysis of equilibrium ion exchange data.$^{(2)}$

In the membrane method, two solutions are placed in a cell on opposite sides of a cation permeable membrane that is presaturated with one of the lanthanides, Ln_b^{3+}. One solution contains $NaNO_3$ (0.1 to 0.5M) and Ln_b^{3+} (0.001 to 0.003M); the other contains the same constituents plus the complex Ln_bY^- (~0.01M). Tracer amounts of a radioactive isotope of the other lanthanide, Ln_a^{3+}, are added to either solution and the cell is shaken at constant temperature until equilibrium is attained.

At equilibrium, the total concentration of the tracer ($\Sigma\, Ln_a$) in either solution can be written

$$(\Sigma\, Ln_a) = (Ln_a^{3+}) + (Ln_aY^-) \qquad (2)$$

(Ln_aY^-) can be expressed in terms of (Ln_a^{3+}), (Ln_b^{3+}), (Ln_bY^-), and the equilibrium constant K for Reaction 1.

$$(Ln_aY^-) = K(Ln_a^{3+})\,\frac{(Ln_bY^-)}{(Ln_b^{3+})} \qquad (3)$$

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(1) R. M. Wallace, J. Phys. Chem. 71, 1271 (1967).

(2) R. H. Betts and O. F. Dahlinger, Can. J. Chem. 37, 91 (1959).

Combination of 2 and 3 yields

$$(\Sigma\ \mathrm{Ln_a}) = (\mathrm{Ln_a^{3+}})[1 + K(\mathrm{Ln_bY^-})/(\mathrm{Ln_b^{3+}})] \tag{4}$$

At equilibrium, an Equation 4 is valid for the solution on each side, R and L, of the membrane; therefore, the ratio of total concentrations of $\mathrm{Ln_a}$ (and hence the R/L radioactivity ratio) is given by

$$r = \frac{(\Sigma\ \mathrm{Ln_a})_R}{(\Sigma\ \mathrm{Ln_a})_L} = \frac{(\mathrm{Ln_a^{3+}})_R[1 + K(\mathrm{Ln_bY^-})_R/(\mathrm{Ln_b^{3+}})_R]}{(\mathrm{Ln_a^{3+}})_L[1 + K(\mathrm{Ln_bY^-})_L/(\mathrm{Ln_b^{3+}})_L]}$$

Donnan equilibrium between the two solutions requires that

$$\frac{(\mathrm{Ln_a^{3+}})_R}{(\mathrm{Ln_a^{3+}})_L} = \frac{(\mathrm{Ln_b^{3+}})_R}{(\mathrm{Ln_b^{3+}})_L} \tag{6}$$

Combination of 5 and 6 yields

$$r = \frac{(\mathrm{Ln_b^{3+}})_R + K(\mathrm{Ln_bY^-})_R}{(\mathrm{Ln_b^{3+}})_L + K(\mathrm{Ln_bY^-})_L} \tag{7}$$

$$K = \frac{r(\mathrm{Ln_b^{3+}})_L - (\mathrm{Ln_b^{3+}})_R}{(\mathrm{Ln_bY^-})_R - r(\mathrm{Ln_bY^-})_L} \tag{8}$$

All quantities except K are measurable:

r is measured from the radioactivity of the two solutions.

$(\mathrm{Ln_b^{3+}})$ in both solutions is determined by titration with EDTA, which is possible because $(\mathrm{Ln_a^{3+}})$ is present only in tracer concentrations, and $(\mathrm{Ln_bY^-})$ does not interfere with the titration because the lanthanide associated with it is already complexed.

$(\mathrm{Ln_bY^-})_R$, the concentration of the complex in the solution into which it was placed originally, is determined by titration with EDTA after oxidation of the complexing agent; correction is made for the free lanthanide originally present.

$(\mathrm{Ln_bY^-})_L$, the concentration of the complex on the side opposite to the one in which it was originally placed, is determined with a Beckman total organic carbon analyzer. This analysis was necessary because, during the time required for equilibration of the cations (~48 to 72 hours at 25°C), about 1% of the complex $(\mathrm{Ln_bY^-})$ leaked from the R side to the L side of the membrane; this concentration is too small to determine by titration with EDTA, but too large to ignore.

Preliminary measurements were made of the equilibria of cerous ion with lanthanum-EDTA and praseodymium-EDTA complexes at 25°C. In both cases, cerous ion was at tracer concentration and the other lanthanide was the macro component. Ionic strength was varied from 0.1 to 0.5M, and some equilibrium concentrations were measured with different ionic strength on opposite sides of the membrane.

The results in the following tables show only small variations in equilibrium constants with ionic strength, as expected for reactions in which the reactants and products have the same charge. Thus, Equation 6 is valid over a wide range of conditions. Although the equilibrium measurements do not require precisely equal ionic strength on the opposite sides of the membrane, approximate equality is desirable to minimize second-order effects such as changes in the ion size parameters.

Stability constants of additional lanthanide and actinide complexes are being measured, for design of rapid ion exchange systems for actinide purification (October report p 23).

Equilibrium Constant at 25°C

$$Ce^{3+} + La(EDTA) \rightarrow Ce(EDTA) + La^{3+}$$

$NaNO_3$, M		La^{3+}, 10^{-3} M		La EDTA, 10^{-3} M		Ce_R/Ce_L	K
R	L	R	L	R	L		
0.1	0.1	2.63	1.82	9.77	0.170	13.16	2.83
0.3	0.3	3.05	2.53	9.85	0.173	10.29	2.85
0.5	0.5	3.66	3.09	9.94	0.155	9.40	2.99
0.1	0.2	1.35	3.36	9.85	0.075	8.67	3.02
0.2	0.3	2.13	3.19	9.58	0.148	8.86	3.15
0.2	0.4	1.76	3.72	9.84	0.133	7.96	3.17
						Avg	3.00 ±0.14

Equilibrium Constants at 25°C

$$Ce^{3+} + Pr(EDTA)^- \rightleftharpoons Ce(EDTA)^- + Pr^{3+}$$

$NaNO_3$, M		Pr^{3+}, 10^{-3} M		$Pr(EDTA)^-$, 10^{-3} M		Ce_R/Ce_L	K
R	L	R	L	R	L		
0.1	0.1	3.03	2.17	9.13	0.204	2.899	0.382
0.3	0.3	3.39	2.85	9.01	0.235	2.325	0.382
0.5	0.5	3.85	3.40	9.14	0.193	2.162	0.401
0.1	0.2	1.59	3.66	9.26	0.172	1.397	0.391
0.2	0.3	2.38	3.60	9.29	0.193	1.665	0.403
0.2	0.4	2.05	4.18	9.52	0.149	1.397	0.407

ION EXCHANGE MEMBRANE SEPARATIONS

In the program to develop a plant-scale ion exchange membrane dialyzer to concentrate dilute uranyl nitrate solutions, a 19-channel dialyzer with nine parallel feed channels was assembled and tested successfully. This apparatus contains nine times the previous total membrane area, and is the first to contain more than one feed channel. The principal problem in scaleup is the design of spacers for the flow channels which must provide uniform parallel flow with no crossleakage.

In one test, uranyl nitrate was concentrated from 0.01 to 0.22M at a rate of 1 kg/day; in a second test, the residual uranium in the raffinate was concentrated to ~0.017M with overall dialysis of 99.9%. Uniform parallel flow in the nine feed channels was demonstrated by a pressure drop in each channel equal to that in the single-channel, two-membrane laboratory dialyzer at equivalent feed rate. Thus, the present dialyzer could be used in the recycle process described in the June 1965 report p 59.

The 19-channel dialyzer has the same channel dimensions as in the laboratory apparatus (July report p 56). In the laminated spacers, a slotted 15-mil polyethylene sheet is fused to the central stainless steel screen with a modified plastic-bag sealer.

A unitized spacer is being developed, and semiworks tests are continuing, to optimize feed rates.

ION EXCHANGE MEMBRANE SEPARATIONS

In the program to develop a plant-scale ion exchange membrane dialyzer (July 1968 report p 56), evaluation of alternative membranes was begun with the laboratory dialyzer and with a new small transport cell for screening tests. An experimental perfluorosulfonic acid membrane was found to be superior to the best previous membrane.

In the small transport cell, a 3.8-cm-diameter membrane separates two compartments, each having a sampling port and a stirring port. The cell is used to measure anion leakage, osmotic flux, and uranium transport. Membranes tested were Du Pont XR experimental perfluorosulfonic acid resin, "AMFion"* C-103, and "Neosepta"** CH-2T and CL-25T.

The rates of transport of uranyl and hydrogen ions were measured with 3M nitric acid in one compartment and 0.1M uranyl nitrate in the other. In other tests, one compartment was filled with 3M nitric acid and the other with water; osmotic flux was measured in the acid compartment; anion leakage as a function of pH, in the water compartment.

Results, summarized in the following table, were calculated as follows. Superior performance is indicated by smaller K_a/K_u and K_w/K_u ratios in the last two columns; measured K_a, K_u, and K_w for the XR resin are inversely proportional to membrane thickness, as expected.

K_w, the osmotic flux parameter, is a measure of the flow of water through a membrane from pure water into nitric acid solution:

$$K_w = \phi_w/A\overline{C}$$

where ϕ_w = flux of water, g/min
A = area of membrane, cm^2
$\overline{C}$ = avg concentration of nitric acid, M

K_a, the nitric acid flux parameter, is a measure of the leakage of nitric acid through the membrane into water:

$$K_a = \phi_a/A\overline{C}$$

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** Trademark of Tokuyama Soda, Tokyo

where ϕ_a = flux of nitric acid, mmole/min

K_u, the uranium flux parameter, is a measure of the maximum exchange flux of uranyl and hydrogen ions through the membrane:

$$K_u = (\phi_u)_{max}/A$$

where $(\phi_u)_{max}$ = flux of uranium, mmole/minute, through membrane when one surface is saturated with uranyl ion, the other with hydrogen ion.

Comparison of Cation Exchange Membranes

	Thickness, mils	K_a, 10^{-4} cm/min	K_w, 10^{-4} g cm/(min)(mmole)	K_u, 10^{-4} mmole/(min)(cm)	K_a/K_u	K_w/K_u
Du Pont XR	5.4	3.9	11.3	16.5	0.24	0.69
	10	2.2	6.6	9.1	0.24	0.72
"Neosepta" CH-2T	7	1.3	4.7	5.0	0.26	0.94
"Neosepta" CL-25T	-	1.3	3.9	4.9	0.26	0.80
"AMFion" C-103	5.7	2.8	4.1	6.2	0.45	0.66

In tests with the laboratory dialyzer, uranyl nitrate was concentrated by Du Pont XR resin from 0.01 to 0.30M, with 3% loss of feed to raffinate. Losses with "AMFion" C-103 were 6 to 8% at 0.25M product. "Neosepta" membranes have a fabric-like structure that is not compatible with present spacer design; edge sealing will be tried.

Other commercial membranes will be tested, and the effect of gamma radiation on flux parameters will be measured in the new transport cell.

ION EXCHANGE MEMBRANE SEPARATIONS

In the program to develop a plant-scale ion exchange membrane dialyzer, tests with two dialyzers in series showed that Du Pont XR experimental perfluorosulfonic acid membrane (July 1968 report p 55) is capable of processing the goal of 6 kg of ^{233}U per day in a 24-membrane laboratory dialyzer. A complete dialysis process for concentrating uranium was described in the October 1965 report p 83.

Each experimental dialyzer has one feed channel, separated from each of two stripping channels by a membrane 10 mils thick by 5 cm wide by 82 cm long.

The XR membrane was tested successfully with feed flow up to 1.2 moles/(hr)(m^2) or 9.6 ml/(min)(100 cm^2); the dialysate from the first dialyzer contained 85% of the uranium from 0.02M feed. This uranium flow is equivalent to the goal rate of 6 kg per day with 24 membranes of this area, and is four times the limit of uranium processing at 85% dialysis with the previous membrane, "AMFion"* C103.

The XR membrane was tested in two dialyzers in series, one to concentrate 0.02M uranyl nitrate and one to strip residual uranium; previously, each operation was demonstrated separately. The following table summarizes tests with three flows in the stripping dialyzer. Overall dialysis approached 99.9%.

The XR membrane is being tested for removal of activity from dilute waste, such as condensate from evaporators for which zeolite columns are now used. Radiation tests of the membrane are in progress.

Concentration and Stripping of Uranium

Feed 0.02M $UO_2(NO_3)_2$
4.6 ml/(min)(100 cm^2)
0.74 mole/(hr)(m^2)
Strip 3M HNO_3
First dialysate 0.35M $UO_2(NO_3)_2$

Second Strip Flow, ml/(min)(100 cm^2)	Second Dialysate U, M	Overall U Dialysis, %
0.16	0.037	99.87
0.23	0.025	99.88
0.29	0.021	99.89

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ION EXCHANGE MEMBRANE SEPARATIONS

Tests show that Donnan dialysis is a promising alternative to zeolite columns (October report p 97) for removing ^{137}Cs from evaporator distillates. Removal factors were 2000; 100 is acceptable. In addition, ^{144}Ce was removed by a factor of 25, $^{103-106}$Ru by a factor of 100, and ^{95}Zr-^{95}Nb by a factor of 50. These nuclides are not removed by zeolite.

In the tests, plant evaporator distillate was fed to the single feed channel of a laboratory dialyzer (November report p 40). The distillate contained about 0.01M NH_4NO_3, 0.001M $NaNO_3$, 6000 pCi/ml ^{137}Cs and traces of other radionuclides. Area of the experimental perfluorosulfonic acid membrane (DuPont XR) was 820 cm^2; feed flows were 40, 45, and 50 ml/min; respective stripping flows of 3M HNO_3 were 0.50, 0.40 and 0.32 ml/min.

The tests show that activity from a feed flow of 10,000 gal/day can be concentrated to ∿200 gallons in 1M HNO_3, with a cesium removal factor of 1600; greater reduction in volume can be obtained with smaller, but adequate, removal of cesium.

Similar tests are planned with the distillate from the separations general purpose evaporator, in which the principal activity is ^{137}Cs, and with water from the reactor vertical tube storage basins, which contains a variety of activities.

ION EXCHANGE MEMBRANE SEPARATIONS

In the program to develop a plant-scale ion exchange membrane dialyzer to concentrate uranium, processing rate was quadrupled by increasing temperature from 22.5 to 70°C. At the higher temperature, the goal of 6 kg of ^{233}U per day can be processed with 8 to 12 membranes instead of the 24 predicted from tests at room temperature (November 1969 report p 40).

A Donnan dialyzer was assembled with a single 225-cm^2, 10-mil Du Pont XR perfluorosulfonic acid membrane, which is serviceable up to 125°C. The alternative membrane material, sulfonated polystyrene-polyethylene ("AmFion"*-C103) is oxidized rapidly at 70°C. Uranyl nitrate was concentrated as follows:

Concentration of Uranyl Nitrate

Feed 0.02M

Temperature, °C	22.5	50	70
Feed flow, ml/(min)(100 cm^2)	4.6	14.2	20.3
Uranium concentrated, % of feed	85	81	83
Uranium in product, M	0.27	0.37	0.37

The effect of higher temperature will be measured on the removal of ^{137}Cs from the distillate from the plant waste tank evaporator (December 1969 report p 50).

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* Trademark of American Machine and Foundry

ENVIRONMENTAL STUDIES

Purification of Evaporator Distillate by Ion Exchange Dialysis

In a 35-day plant test, a cation exchange membrane dialyzer decreased cesium activity from 10,000 dis/(min)(ml) to ∿50 and mercury from ∿1000 ppb to ∿3 in distillate from the H Area evaporator that concentrates aged supernate from high activity waste. Feed flow through the dialyzer was 100 gal/day (∿1% of the total flow of distillate). The volume of stripped-ion solution for recycle is ∿3% of feed volume. The results agree with laboratory tests (December 1969 report p 50). Continuing development of larger dialyzers is directed particularly toward removing ionic impurities from streams to seepage basins.

The dialyzer was developed in the laboratory on the basis of Donnan membrane equilibrium (May 1963 report p II-18).[1] In the dialyzer, cations are exchanged between the feed and stripping solutions that flow in opposite directions at controlled rates on opposite sides of the membrane; anions are mutually excluded. The 10-mil membrane is a fluorocarbon material extremely resistant to chemical attack-- Du Pont XR 170 perfluorosulfonic acid copolymer.

Less shielding is needed for a high capacity dialyzer than for ion exchange columns of equal capability, because the strip stream that contains dialyzed material is discharged continuously; but, in columns, activity accumulates until eluted.

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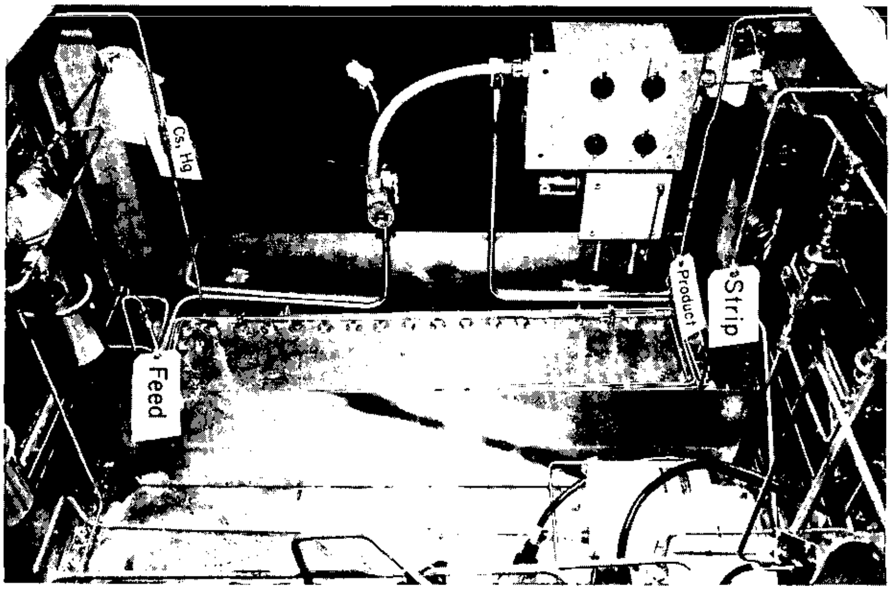
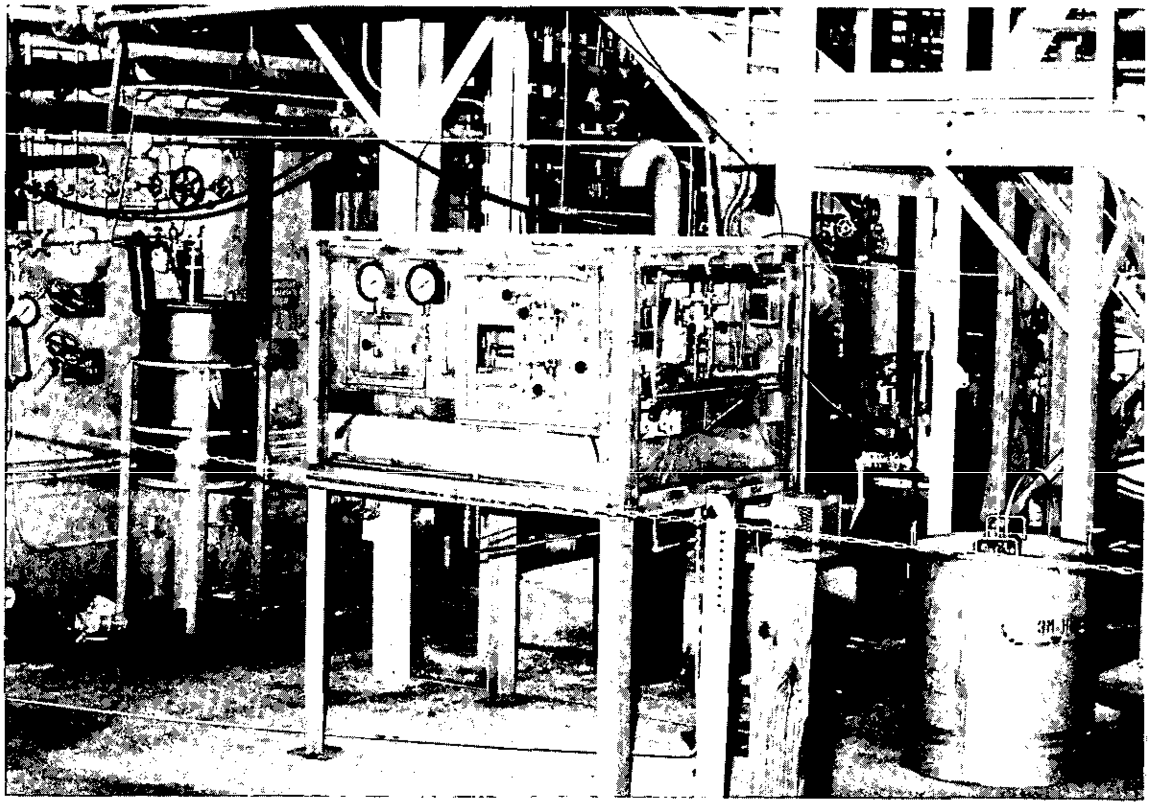
[1] US Patent 3,454,490



Dialyzer in Rack



Plant Test

FIG. 21 100-GAL/DAY DIALYZER

The 100-gal/day dialyzer is operated at 75°C in a thermostated water bath; four times as much feed is dialyzed effectively at 75° than at 25. A portable rack contains the dialyzer, water bath, pumps, and related equipment (Figure 21). Each 20-mil-thick polypropylene plastic frame that forms a flow channel (Figure 22) contains a 12-mil-thick 40-mesh stainless steel screen to support the 10-mil membrane. Membrane area for cation exchange is 5 by 35 inches. Thickness of the feed channel is maintained constant and uniform by a small positive pressure in the strip channel that presses the membrane against the 12-ml screen in the feed channel (Figure 23). With this feed channel thickness, ions diffuse to the membrane in less time than they diffuse through the membrane. Feed residence time in the dialyzer was only 10 seconds.

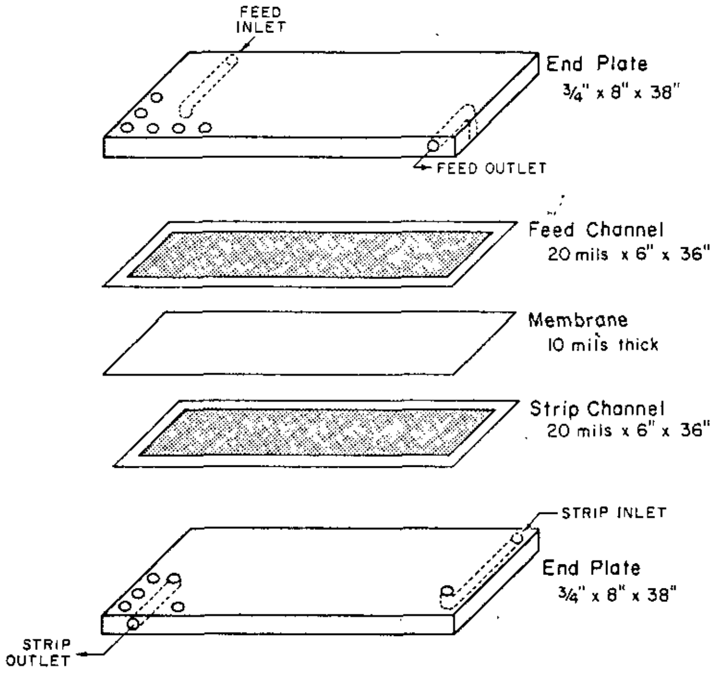


FIG. 22 DIALYZER COMPONENTS

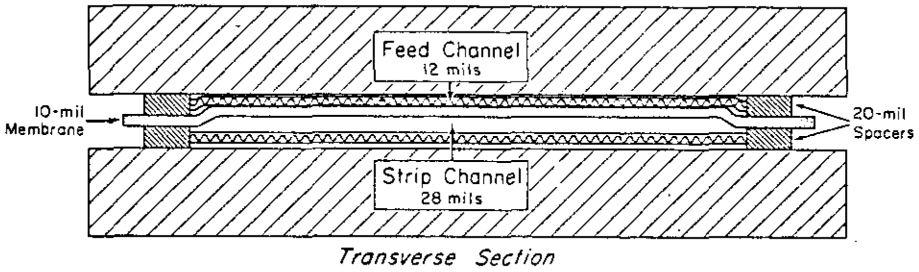


FIG. 23 STRIP PRESSURE ASSURES UNIFORM DIFFUSION DISTANCE

The feed contained 0.01M NH_4OH and as much as 10^5 dis/(min)(ml) of ^{137}Cs ($\sim 10^{-9}$M) and 0.5 to 1.3 ppm of Hg. The feed was filtered to remove 20-µ particulate material, and was fed to the dialyzer at 100 gal/day; cesium and other cations were stripped with 0.9 gal/day of 3M HNO_3. ^{137}Cs activity was stripped by a factor of 850 from feed containing 10^5 dis/(min)(ml), and by a factor of 20 from feed containing 200 dis/(min)(ml) (Figure 24). The wide range of feed activity enlarged the scope of the successful test. About 2 gallons of water per day diffused into the strip channel by osmosis. Thus, the volume of stripped-ion solution for recycle is ∿3% of the dialyzer feed.

Mercury was dialyzed simultaneously with a removal factor of ∿500, to 1-3 ppb. The evaporator distillate contains filterable mercury metal and mercury ions (or species in rapid equilibrium with ions). The dialyzer removes only ionic species; filtration is summarized in the following section.

Initial pressure drop through the feed channel at 100 gal/day (270 ml/min) was 23 psig. During 3 weeks, the pressure increased to 50 psig. Flow direction was then reversed in both channels; feed pressure decreased to 26 psig and remained low throughout the remaining 2 weeks. The pressure increase is attributed to small particles caught in the 40-mesh screen. A 1-µ feed filter is being evaluated.

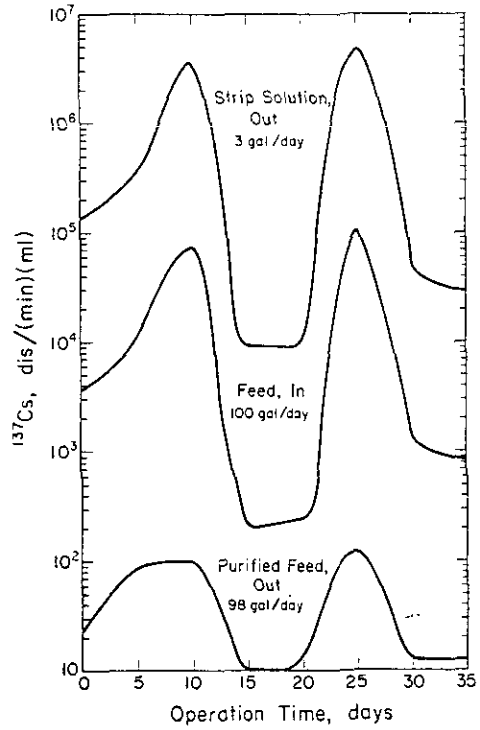


FIG. 24 THIRTY-FIVE DAY DIALYSIS OF ^{137}Cs

Operation of the 100-gal/day dialyzer will be continued with evaporator distillate to determine the life of the initial membrane, possibly at temperatures up to ∿100°C and at the proportionately higher flows. Plant tests in other applications are being planned for similar dialyzers.

Dialyzer scaleup to 10,000 gal/day is planned. Membrane area would be increased by stacking spacers and membranes between the end plates, with internal manifolding to provide uniform parallel flow (Figure 25). A 10,000-gal/day dialyzer containing 140 membranes would be about 6 inches high, 8 inches wide, and 38 inches long -- well within the range of fabrication of electrodialyzers, which contain up to six hundred 36-inch-square membranes. Large ion exchange dialyzers are expected to remove metal-ion contaminants (such as Pb, Hg, Cd) effectively from commercial waste effluents of low total salt concentration.

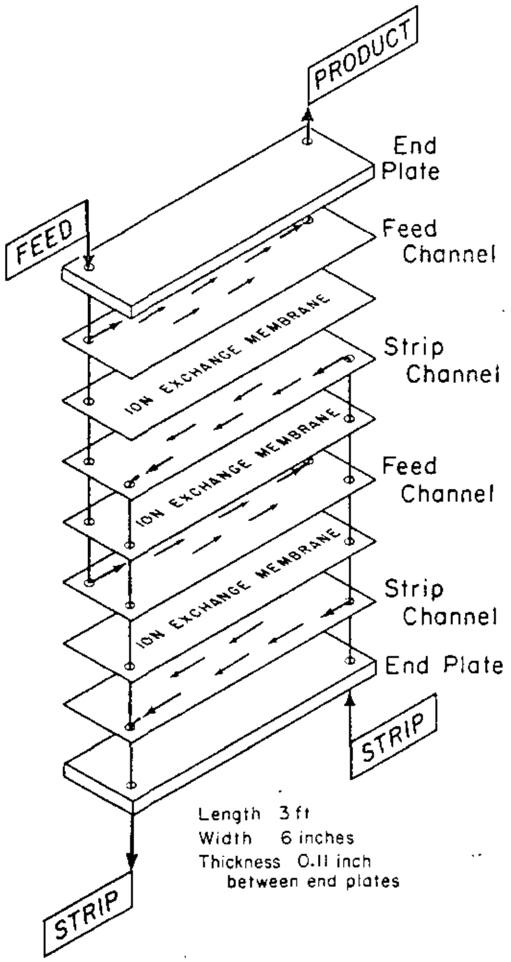


FIG. 25 DIALYZER SCALE UP

Decontamination of Evaporator Distillate by Filtration

The 20-μ "Dynel"* yarn filter cartridge used to filter feed for the foregoing dialyzer operation retained particulate material containing 8 ±4 mCi of activity from 1400 gal of the evaporator distillate. 40 g of metallic mercury was also retained by the filter. These data indicate that filtration may extend the life of the zeolite column currently used to remove ^{137}Cs from distillate and may be useful for cleanup of other plant effluent streams.

Radiation was 3 mR/hr 3 feet from the filter cartridge; 50% was ^{106}Ru; 25%, ^{95}Nb; 15%, ^{95}Zr; 10%, combined ^{144}Ce, ^{125}Sb, ^{103}Ru, ^{154,155}Eu, and ^{60}Co. Some of these nuclides originated from waste solutions from the regeneration facility for portable deionizers, temporarily added directly to the evaporator feed tank during 1971. On the basis of these data, the 136,000 gallons of distillate produced during the period of filtration apparently contained ∿0.6 Ci of filterable activity.

Potential applications of filtration are being considered for decontaminating various plant effluents.

ENVIRONMENTAL STUDY

Purification of Reactor Basin Water by Ion Exchange Membrane Dialysis

Cationic radionuclides in reactor disassembly basin water were removed effectively by Donnan dialysis with ion exchange membranes in laboratory tests. Cations were exchanged between the feed and stripping solutions that flow in opposite directions at controlled rates on opposite sides of a cation exchange membrane; anions are mutually excluded. Anions could be removed by a dialyzer with a membrane that exchanges anions. Exchange membrane dialysis was demonstrated previously to remove ^{137}Cs and mercury from waste evaporator condensate (January 1972 report p 77).

The reactor disassembly basin stores fuel and target assemblies in water after discharge. Small amounts of tritium and nonvolatile radionuclides transfer from the assemblies into the basin water. Tritium is now removed by purging water from the system; radionuclides, by columns of ion exchange resins.

The tests used a 10-mil membrane of "Nafion"* which is extremely resistant to chemical attack. Reactor basin water was fed to a single cationic membrane dialyzer at 75°C and 8.7 ml/(min)(100 cm^2). A 3M HNO_3 strip solution was used at 1% of basin water flow in one series of tests; 1/2% in a second series. Cations were exchanged into the strip stream during dialysis. Data are tabulated below.

^{134}Cs and ^{137}Cs were negligible in the treated basin water (dialysate). The behavior of ^{95}Zr-^{95}Nb, ^{144}Ce, and ^{51}Cr was not defined clearly because the basin water used in these tests contained lower than usual concentrations. Further tests will include normal concentrations of all radionuclides and will also test higher flows per unit membrane area and other feed/strip ratios.

---

* Du Pont trademark for perfluorosulfonic acid copolymer

Removal of Radionuclides from Reactor Basin Water by Ion Exchange Membrane Dialyzer, dis/(min)(ml)

Feed 8.7 ml/(min)(100 cm^2)
Temp 75°C

		Strip = 1% of Feed		Strip = 1/2% of Feed	
	Feed	Effluent Strip	Dialysate	Effluent Strip	Dialysate
^{51}Cr	51	-	20	-	20
^{54}Mn	1.7	24	0.05	35	-
^{58}Co	13	180	0.5	260	0.4
^{60}Co	3.1	44	-	67	-
^{65}Zn	12	210	-	300	-
^{134}Cs	69	1500	-	2200	-
^{137}Cs	115	2200	-	3300	0.5
^{140}Ba	12	300	-	640	-
^{144}Ce	0.4	-	-	-	-

\- denotes below sensitivity of analysis

WASTE MANAGEMENT

Cleanup of Waste Evaporator Distillate by Membrane Ion-Exchange

Study has continued of Donnan dialysis for separating and concentrating ionic species, with emphasis on improving the process and equipment to increase the efficiency of a prototype dialyzer for removing cesium from H Area waste evaporator distillate (January 1972 report p 77). Improvements include:

Increasing the thickness of the dialyzer channel from 13 to 28 mils to decrease the pressure drop and membrane pluggage with only moderate decrease in ion transport rate.

Using an electrical feed heater to improve control and eliminate humidity problems associated with previous water-bath heating of the dialyzer.

In addition, mathematical models were developed that provide useful computer evaluation of alternative designs, particularly for the uranyl nitrate-nitric acid system.

Equipment Modifications

During a 35-day plant test (January 1972 report p 77) of cation exchange dialysis for removing cesium activity from H Area waste evaporator distillate, pressure drop across the feed channel became excessive due to buildup of solid material in the feed port manifolds and spacer screen. This required occasional shutdown for system backflush. Two modifications were tested to solve this problem:

Existing 20-micron filters were replaced with a 1-micron filter to increase predialysis filtration. This helped, but not enough.

Pilot-scale tests with water indicated that increasing the channel thickness reduces the pressure drop (first table below).

The transport rate is only slightly diminished if the number of membranes is increased to compensate for the increased channel thickness; thus laboratory measurements (second table) indicate that a 28-mil-channel dialyzer with 2 membranes performs about as well as a 13-mil-channel dialyzer with 1 membrane.

Plant tests are expected to show less pluggage with thicker channels. Other advantages of increased spacer thickness are significant improvements in manifold port design allowed by the greater frame thickness (35 mils); easier, lower-cost fabrication of spacers; and enhanced safety because of the reduced operating pressure.

Replacement of the hot water bath for heating the dialyzer by an electrical or steam preheating system for the feed allowed better control of dialyzer temperature and eliminated the high humidity (detrimental to instruments in the dialyzer cabinet). Electrical preheaters are currently favored for feed flows <2 gpm.

An endurance test is planned for a pilot-scale dialyzer with 28-mil channels and 2 membranes; continuing ability to strip ^{137}Cs, mercury, and other ions from H Area waste evaporator distillate will be tested, to evaluate the foregoing design changes. A second pilot-scale dialyzer with 4 membranes (2 feed channels and 3 strip channels) is nearly ready for plant testing with other aqueous effluents.

Effect of Channel Thickness on Feed-Channel Pressure Drop

Spacer:	20-gauge stainless steel, 6" x 36"
Screen:	20-mesh stainless steel, 5" x 32"
Strip Pressure:	5 psig > feed channel inlet pressure

Feed Flow, ml/min	Channel Thickness, mils	Pressure Drop, psig
540	13	42
540	28	13
540	40	3
1080	13	>100
1080	28	31
1080	40	7

Effect of Channel Thickness, Number of Membranes, and Temperature on Dialyzer Performance

Feed: 0.02M $UO_2(NO_3)_2$, ∿5.0 ml/(min)(100 cm^2)
Strip: 3.0M HNO_3, ∿0.05 ml/(min)(100 cm^2)

Channel Thickness, mils	Number of Membranes	Temp, °C	$UO_2(NO_3)_2$ Remaining in Feed, %	$UO_2(NO_3)_2$ Strip Outlet Conc, M
13	1	22	15.1	0.282
28	2	22	20.1	0.258
13	1	75	1.4	0.233
28	2	75	2.5	0.226

Mathematical Modeling

Theoretical analysis of the continuous Donnan dialysis separation process is being compared with experimental measurements to develop a mathematical model that will allow optimizing the design of a parallel-channel dialyzer by computer simulation. The current model is based on steady-state differential mass balances in flow channels coupled to the Donnan membrane equilibrium equation and to membrane flux equations describing the transport of the feed counter-ion (uranyl or sodium cation, for example), the solvent (water), and the co-ion (such as nitrate).[1] The mass transfer rate of the counter-ion is based on a membrane-phase driving force, while the solvent and co-ion fluxes are related directly to concentrations in the bulk fluid phases.

Values of mass-transfer coefficients for osmotic, co-ion, and counter-ion fluxes were determined by fitting empirical equations to operating data measured in the laboratory. Correlations for the uranyl nitrate-nitric acid systems were of the form

$$k = \alpha\, u_f^{\beta} \exp(-\gamma/T)$$

where k = mass transfer coefficient
u_f = feed channel velocity
T = temperature
α, β, γ = adjustable parameters

Comparison of calculated dialyzer performance based on these mass transfer coefficients with measured performance indicates that the mathematical simulation is satisfactory for the uranyl nitrate - nitric acid system to be used for evaluating alternative dialyzer designs. Typical results are shown below.

Calculated vs Measured Dialyzer Performance

Feed: 0.019M $UO_2(NO_3)_2$, 49 ml/min
Strip: 3.0M HNO_3, 0.49 ml/min
Dialyzer: 2¼" x 32", 2 membranes, 25°C

	Composition, M	
	Calculated	Measured
Waste	0.00355[a]	0.00395[b]
Product	0.267	0.264

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[a] 19% of uranium in feed
[b] 21% of uranium in feed

Calculated design modifications shown in the last 2 lines of the next table indicate improved performance over the current design, line 1.

Design Calculations - Constant Membrane Area

Feed: 0.019M $UO_2(NO_3)_2$, 75°C, 20 liters/min
Strip: 3.0M HNO_3, 0.5 liter/min

Size	Membranes	$UO_2(NO_3)_2$ Remaining in Feed, %	$UO_2(NO_3)_2$ in Strip, M
5" x 32"	368	6.3	0.234
10" x 32"	184	6.3	0.234
10" x 16"	368	22	0.178
5" x 64"	184	<1	0.268
5" x 32"	368[a]	5.0	0.165

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[a] like first case except 1.5 liters/min of 1.0M HNO_3 strip

However, results obtained with the univalent sodium nitrate - nitric acid system were poor. The counter-ion transport equation based on the membrane-phase driving force appears inadequate. Because the velocity dependence of the mass transfer coefficients of the uranyl nitrate system indicates that the major resistance to cation transport lies in the flow channels, the model is being extended to include liquid film resistance. A multiple-resistance model which takes into account both liquid film and membrane resistances will be formulated. Initial modifications have improved the correlation with sodium nitrate data; further improvement is needed for design use.

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1. S. S. Melsheimer, H. M. Kelley, L. F. Landon, and R. M. Wallace. "A Theoretical and Experimental Study of Donnan Dialysis, A *Continuous Ion* Exchange Membrane Process." Paper presented at the 74th National AIChE Meeting, New Orleans, La., March 12, 1973.

OSR-24-A117
(REV. 7-65)

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E. I. du Pont de Nemours & Company
INCORPORATED
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29802
(TWX: 803-824-0018, TEL: 803-824-6331, WU: AUGUSTA, GA.)

BCC: I. A. Hobbs, SROO
R. G. Erdley
S. A. McNeight, Wilm.
C. H. Ice-L. H. Meyer, SRL
TIS Record Copy

December 30, 1965

Dr. B. L. Baker, Chairman
Department of Chemical Engineering
University of South Carolina
Columbia, South Carolina

Dear Dr. Baker:

DPST-65-301, 3rd Supplement

The enclosed report, pages 70-79, describes R. M. Wallace's recent work on ion exchange membranes.

This material is to be bound with that transmitted by my letter of May 26, 1965, and numbered DPST-65-301.

Very truly yours,

HM Kelley
H. M. Kelley
Separations Chemistry Division

HMK:ag
Encl.

DSR-24-A117

2978

DPST-65-301

BCC: I. A. Hobbs, SROO
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EXPLOSIVES DEPARTMENT
SAVANNAH RIVER LABORATORY

August 9, 1965

Dr. B. L. Baker, Chairman
Department of Chemical Engineering
University of South Carolina
Columbia, South Carolina

Dear Dr. Baker:

DPST-65-301, 1st Supplement

The enclosed report describes R. M. Wallace's recent work on ion exchange membranes.

This material is to be bound with that transmitted by my letter of May 26, 1965, and numbered DPST-65-301.

Very truly yours,

H. M. Kelley
Separations Chemistry Division

HMK/fy
Encl.

ION EXCHANGE MEMBRANE SEPARATIONS

Study was continued of the concentration of uranyl nitrate solutions by "Donnan dialysis processes", which are based on the approach to Donnan membrane equilibrium. As described in the March report, this technique is quite adaptable to continuous operation, which is a potential advantage over the current method of concentration by ion exchange resin columns in typical B-Line operations.

Tests were made with a 23-membrane countercurrent concentrator with "AMFion"* C103 membranes and with nitric or sulfuric acid as the uranium stripping solution. For a given stripping solution, the final concentration of uranium in this solution and the loss of uranium in the stripped feed solution were determined by two operating conditions: the absolute flow of the feed and the stoichiometric flow ratio between the stripping solution and the feed. The tests also confirmed predictions that sulfuric acid is a more effective stripping agent than nitric acid, and that the loss of uranium in the stripped feed is interdependent with the concentration of uranium in the product.

A method was devised for circumventing the association of high losses in the stripped feed with high concentrations in the product. The uranium is first concentrated to a high value with relatively high "loss" in the stripped feed. The latter is then processed through a second cation membrane separator, which strips essentially all of the residual uranium and concentrates it to the original feed value for recycle to the first concentrator.

As described in the March report, the maximum conceivable concentration of uranium in the product from a countercurrent separator is attained when $2U_Fg_F = C_og_o$

where U_F = concentration of uranium in the feed
g_F = flow rate of the feed
C_o = molar concentration of nitric acid in stripping solution
g_o = flow rate of stripping solution.

Under these conditions, the nitrate ion fed to the separator in the strip solution is just sufficient to accommodate the uranium in the feed solution. This condition implies that the ratio $\alpha \equiv C_og_o/2U_Fg_F$ is an important operating parameter for membrane separators, because it is a measure of the stoichiometric saturation of the product solution with respect to uranium when all of the uranium is removed from the feed solution. Thus, the value of α is an index of the approach to conditions that will yield maximum concentration. The rate of feed

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* Trademark of American Machine and Foundry Co.

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flow is also important, because it determines the residence time of the feed within the separator and hence the time available for the stripping process.

Concentrating System for Donnan Dialysis

Tests with Nitric Acid Stripping Solutions

The results of tests with the 23-membrane separator, in which 0.01M uranyl nitrate in the feed was stripped with 2M nitric acid, are shown in the following table. The feed rate was constant within separate groups of the tests in which the value of α was varied. Each test was operated for at least 7 hours.

Steady state was attained in all tests except the first two at feed rates of 5 ml/min, in which α was 1.0 and 0.8. The attainment of steady state was demonstrated by determining the uranium concentration in the stripped feed at various times.

The loss of uranium in the stripped feed decreased with increasing values of α at constant feed rate; the concentration of uranium in the product remained fairly constant up to $\alpha = 1.5$, then decreased with further increase in α. The loss of uranium decreased with decreasing feed rate at constant α, as expected. The concentration of free acid (H^+) in the product increased with increasing α and was close to the concentration predicted from the excess acid added in the strip. The free acid remaining in the stripped feed from all tests was slightly higher than that predicted for a simple exchange of hydrogen ion for uranyl ion. This observation indicates that a small amount of nitric acid diffuses through the membranes. The diffusion is also indicated by the small increase in free acid in the stripped feed as α is increased and the feed flow is decreased.

The values of K (the parameter related to the osmotic transport of water as described in the March report) varied considerably with α. This variation is attributed to a greater degree of saturation of the membranes with uranyl ion for the small values of α. In the tests for which α was 0.8 and 1.0, nearly all of the membranes were saturated with uranium. For large α, only the membranes in the first few stages were saturated. The variations in K can be explained on the basis that the membranes saturated with uranyl ion transport water less readily than the membranes that are in the hydrogen form. The experimental values of K for the larger values of α agree fairly well with the value of 0.012 that was reported in March from tests with the 11-membrane separator.

Concentration of Uranyl Nitrate in 23-Membrane Separator with Nitric Acid

Feed $U_F = 0.01M\ UO_2(NO_3)_2$; (no HNO_3)
Stripping Solution $C_o = 2.0M\ HNO_3$

Flow, ml/min							H^+, M	
g_F (Feed)	g_o (Strip)	g_p (Product)	α(a)	K(b)	Product UO_2^{2+}, M	Stripped Feed UO_2^{2+}, %	Product	Stripped Feed
5.0	0.040	0.0995	0.80(c)	0.00448	0.282	24.6	0.0126	0.0292
	0.050	0.112	1.00(c)	0.00435	0.274	17.8	0.0297	0.0231
	0.060	0.142	1.20	0.00600	0.273	7.46	0.0466	0.0244
	0.075	0.176	1.50	0.00730	0.268	3.34	0.109	0.0270
	0.100	0.230	2.00	0.00930	0.210	1.33	0.269	0.0292
	0.200	0.339	4.00	0.00822	0.148	0.67	0.551	0.0315
4.0	0.060	0.158	1.50	0.00774	0.220	1.41	0.0951	0.0274
	0.080	0.207	2.00	0.00991	0.189	0.56	0.218	0.0293
	0.160	0.314	4.00	0.00987	0.124	0.18	0.534	0.0342
3.0	0.036	0.111	1.20	0.00665	0.189	1.76	0.0207	0.0266
	0.045	0.141	1.50	0.00861	0.185	0.15	0.0726	0.0285
	0.060	0.181	2.00	0.0106	0.155	0.09	0.188	0.0308
	0.160	0.344	5.30	0.0126	0.0838	<0.05	0.596	0.0401

(a) $\alpha = C_o g_o / 2 U_F g_F$

(b) $K = [(C_o/C_n)^2 - 1] / [C_o/g_o]$ where $C_n = HNO_3$ in product, M. (March, Equation 7)
K is a function of the nature and area of the membrane, and of the type but not the concentration of the acid in the stripping solution.

(c) Not at steady state.

Tests with Sulfuric Acid Stripping Solutions

The results of tests with the 23-membrane separator with sulfuric acid as the stripping solution are summarized in the following table. The increase from 1 to 2M in concentration of sulfuric acid in the third group of tests was made after the determined values of K indicated a more concentrated stripping solution would produce a more concentrated product stream for the reasons explained in the March report.

In the first group of tests, the feed flow was constant and α was varied. The definition of α in terms of concentration and flow rates for a stripping solution of sulfuric acid $(C_o g_o / U_F g_F)$ is twice that for a nitric acid strip because only half as many moles of sulfate are required to accommodate the uranium. In all other tests, α was constant at 1.2 and the feed flow was varied.

The general behavior of the membrane separator with sulfuric acid as the stripping solution was much the same as that with nitric acid: the concentration of uranium in the product and the loss in the stripped feed both decreased, with either increasing α or decreasing flow.

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The quantitative behavior, however, differed greatly. The concentration of uranium in the product was consistently higher and the loss in the stripped feed was consistently lower with sulfuric acid than with nitric acid, when both systems were operated at similar conditions. The greater effectiveness of sulfuric acid as a concentrating agent is due to two factors.

> Sulfate ion is a complexing agent for uranyl ion, and therefore permits operation at conditions closer to stoichiometric saturation (smaller α) than can be used with nitric acid. At flow of 5 ml/min and $\alpha = 1.2$, the loss in the stripped feed was only 1.4% when 1M sulfuric acid was used as a stripping agent; in contrast, α was necessarily increased to 2.0 to obtain similarly small loss with 2M nitric acid as the stripping agent. Similarly, when nitric acid was used as the stripping solution, the product concentration remained constant for values of α below 1.5; but with sulfuric acid the product concentration continued to increase for values of α down to 1.2.
>
> A second advantage with a sulfuric acid strip is that osmotic transport of water is less than that with a nitric acid stripping solution for the same values of α. Although the osmotic factor K for sulfuric acid is similar to that for nitric acid in the present system, K enters into the osmotic equation only as a product with C_o, the concentration of the stripping solution, as shown in the March report. Because only half as much sulfuric acid is required to obtain the same value of α, the effective osmotic factor (KC_o) for sulfuric acid is half that for nitric acid.

The concentration of free acid (H^+) in the product was again low, and nearly equal to the values calculated from the excess acid in the stripping solution and the concentration of uranium in the product. The free acid in the stripped feed is very close to the value calculated for simple exchange between uranium and hydrogen ions, which indicates that almost no sulfuric acid was transported through the membranes. The following conclusions were drawn from the foregoing tests.

> Uranium can be concentrated from 0.01M (2.4 g/l) up to ~0.27M (64 g/l) with nitric acid as the stripping solution, or up to ~0.45M (107 g/l) with sulfuric acid as the stripping solution.
>
> The quality of the product solution obtained by the continuous membrane separation is superior to that obtained by conventional ion exchange methods, because the product contains only little excess acid in contrast to the high concentrations of nitric acid or ammonium nitrate obtained in the elution of uranium from ion exchange columns.

of the membrane in contact with the sulfate-perchlorate mixtures and the side in contact with pure perchlorate solutions.

The data from which the equilibrium quotients were evaluated are summarized in the following table. The concentrations of free sulfate ion shown in the third column have been corrected for the small concentration of bisulfate ion. The quantities Q_1 and Q_2 were determined by least squares fit of Equation 3. No evidence was found of complexes higher than the bisulfate.

The enthalpies of the reactions were determined by the conventional plot of log Q vs $\frac{1}{T, {}^\circ K}$. The value of +4.58 kcal/mol for ΔH_1 agrees well with the value of +4.88 at infinite dilution (April report).

Measurements are now being made of the equilibrium quotients for the reactions of uranyl ion with oxalate and ethylenediaminetetraacetate ions, and apparatus is being constructed for the continuous separation and concentrations of ions.

Data for Calculation of Equilibrium Quotients for Uranyl Sulfate Complexes

	U_R/U_L	Na_R/Na_L	(SO_4)	$\frac{R-1}{(SO_4)}$
25°C	3.144	0.957	0.01687	144.2
	5.163	.901	.03469	154.5
	7.479	.846	.05338	177.0
	9.090	.776	.07418	190.0
	9.477	.768	.08359	182.0
	9.856	.721	.09242	194.7
		$Q_1 = 135.1 \pm 6.3$		
		$Q_2 = 654 \pm 97$		
34.2°C	3.816	0.959	0.01609	195.6
	7.27	.905	.03331	236.5
	10.38	.864	.05248	246.0
	13.56	.795	.07490	273.2
	15.19	.789	.08242	283.7
	15.77	.742	.09215	299.7
		$Q_1 = 182.0 \pm 7.4$		
		$Q_2 = 1280 \pm 120$		
47.8°C	4.933	0.963	0.01622	266.3
	10.08	.918	.03247	336.9
	14.87	.871	.05087	365.4
	21.37	.844	.07274	398.7
	24.88	.821	.08329	431.1
	29.97	.788	.09134	482.2
		$Q_1 = 237 \pm 18$		
		$Q_2 = 654 \pm 270$		

ION EXCHANGE MEMBRANE SEPARATIONS

Dilute aqueous solutions of uranyl nitrate were concentrated continuously by use of the Donnan equilibrium across ion exchange membranes. Use of this technique to determine the charges of ions in solution and to measure the complexing constants for uranyl sulfate have been described in the Monthly Reports for May, September, October, and December 1963; and February, April, and June 1964. The technique is now being adapted to specific separations processes such as concentrations of the type that are used for solutions of plutonium and $^{233}UO_2^{2+}$ nitrates in the B Line.

The principal advantage of the membrane technique over the present use of ion exchange resin columns in the B Line is the simplicity of its adaption to continuous operation. The initial tests of the practicality of concentration by the Donnan membrane method are described in the following paragraphs. The results of the tests are encouraging; decontamination obtainable by this technique will be evaluated in later tests.

The apparatus used in the initial concentration tests with uranyl nitrate consisted of six compartments separated by "AMFion"* C103 cation exchange membranes. A feed solution of dilute uranyl nitrate and a strip solution of concentrated nitric acid flowed through alternate compartments. The efficiency of the apparatus was shown to depend on flow, temperature, and the concentration of acid in the strip solution. The highest concentrations of uranyl ion in the product (effluent strip) solution were obtained with 3M HNO_3 at 35°C. The uranyl ion was concentrated from 0.01 to 0.244M (~2.4 to ~58 g/l) and the raffinate concentration was only 0.0013M (0.31 g/l). The total flow was 1 ml/min and the exposed membrane surface area was 11.5 inch^2.

The apparatus is shown schematically in Figure 21. The feed solution is pumped in parallel through the three compartments labeled D; the raffinate stream, in which nearly all of the initial UO_2^{2+} is replaced by H^+, flows from the opposite ends of these compartments. Similarly, the strip solution is pumped through the three C compartments in parallel and the product stream flows from the opposite ends. The frame of each compartment is drilled to provide internal manifolds for routing the two solutions through the D or C compartments, and is equipped with conventional over-and-under baffles that conduct the flowing solutions through the compartments and

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ensure that they do not bypass any of the membrane surface. Each frame also contains transverse baffles that agitate the solutions as they flow through the compartment. Approximately 2.3 inch^2 of each membrane is exposed to the solutions.

The feed and strip streams are each driven by two pumps. One pump advances the solution at up to 3 ml/min and the other pump agitates the solution by pulsing it back and forth at ~40 ml/min.

Several preliminary tests were made in which the feed solution contained 0.01M uranyl nitrate and the strip solution contained 1M nitric acid. The feed flow was varied from 0.5 to 3 ml/min while the strip flow was always 1/10 of the feed flow. Tests were made at 25, 35, and 50°C. Each test was continued ~6 hours in order to reach steady state. The results are shown in the following table.

Continuous Concentration of $UO_2(NO_3)_2$ by Donnan Equilibrium

Initial Concentrations
Feed Stream 0.01M $UO_2(NO_3)_2$
Strip Stream 1.0M HNO_3

Flow, ml/min			Final Concentration of Uranium, Mx10^3		Over-all Stage
Feed	Strip	Temp, °C	Raffinate	Product	Separation
0.5	0.05	25	0.23	68	300
1.0	0.1		0.73	87	120
2.0	0.2		2.5	78	30
3.0	0.3		4.2	67	16
0.5	0.05	35	0.14	69	500
1.0	0.1		0.42	80	190
2.0	0.2		4.2	55	13
3.0	0.3		4.7	54	11
0.5	0.05	50	0.5	104	200
1.0	0.1		1.9	100	50
2.0	0.2		3.6	69	19

These results demonstrate that uranyl ion can be concentrated by the membrane technique and that the efficiency with which uranium is removed from the feed stream depends upon the flow rate and temperature. The best of the three temperatures appears to be 35°C on the basis of the over-all stage separation at 0.5 and 1.0 ml/min. The erratic results at the higher flows (at 35°C) are believed to have been caused by air leaving the solution and blocking some of the channels so that the solutions bypassed some of the compartments.

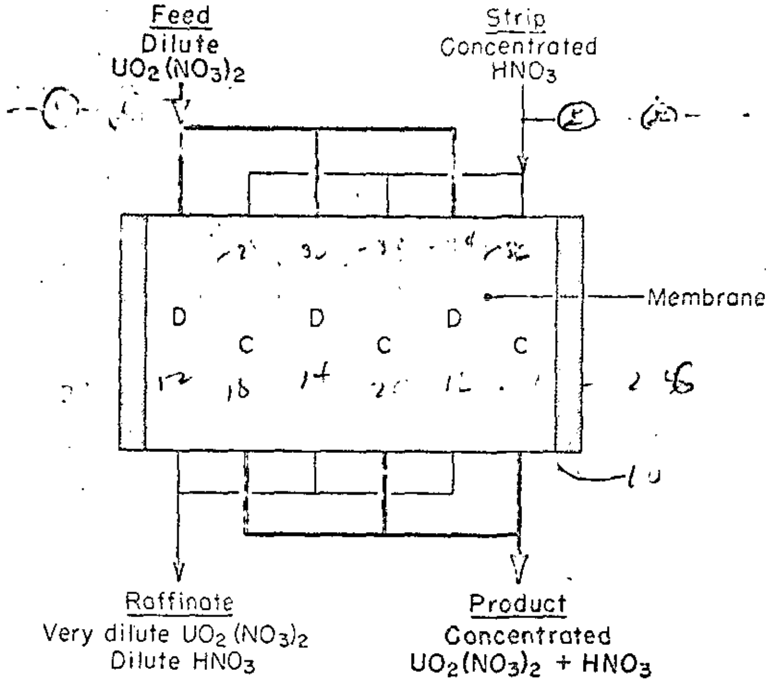

FIG. 21 SINGLE-STAGE CONCENTRATOR

In a second series of tests the strip flow was reduced further in an attempt to increase the concentration of uranyl ion in the product. Two experiments, with 1 and 3M HNO_3 in the strip solution, were continued at 35°C for 24 hours. The results, shown in the following table, demonstate that 3M nitric acid is the more effective concentrating agent.

Continuous Concentration of $UO_2(NO_3)_2$ by Donnan Equilibrium

Initial concentration of feed stream 0.01M $UO_2(NO_3)_2$
Temperature 35°C

Initial HNO_3 in Strip, M	Flow, ml/min		Final Concentration of Uranium, $M \times 10^3$		Over-all Stage Separation
	Feed	Strip	Raffinate	Product	
1	1.0	0.017	5.5	220	40
3	1.0	0.031	1.2	244	200

All tests to date have been made with the single stage apparatus with only 11.5 inch^2 of exposed membrane. Three of these assemblies in series would be expected to reduce the uranium in the raffinate to about 0.2% of that in the feed and to yield a product containing 0.244M (58 g/l) uranium.

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Similarly, a device containing only 240 ft^2 of exposed membrane surface would be expected to process about 3.5 kg of uranium per day. If only 50% of the membrane area is in contact with the solution (part of the membrane area is masked by the baffles) and each compartment is 1/16 inch thick, the dimensions of such a device would be only 2 x 2 x 0.625 ft.

Tests are being made of the concentration of uranyl nitrate from less concentrated solutions to simulate a concentrator for raffinate from the first stage, and with other strip solutions such as ammonium bioxalate or a mixture of nitric acid and ammonium nitrate. A completely countercurrent device, theoretically much more efficient than the present single stage unit, is being designed.

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ION EXCHANGE MEMBRANE SEPARATIONS

Study was continued of the concentration of dilute uranyl nitrate solutions by Donnan membrane equilibrium, as described in the August report. This technique is being studied because of its apparent simplicity of adaption to continuous operation, which is a potential advantage over the current method of concentration with ion exchange resin columns in the B Lines.

Tests with a nine-membrane countercurrent concentrator, using "AMFion"* C103 membranes, showed that uranium can be concentrated from 0.01 to 0.11M. Only 0.05% of the uranium remained in the raffinate. "AMFion" C313 membrane was shown to be about five times as efficient as "AMFion" C103 for concentrating uranyl ion in tests with a single-membrane cell; both of these membranes were more efficient than the others that were tested.

Further tests with the C313 membrane in the single-membrane assembly demonstrated that uranyl nitrate can be concentrated from a solution containing 0.1M nitric acid into 3M nitric acid -- conditions that simulate those expected for the ^{233}U concentration step in the

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plant. Concentration from the solution containing 0.1M nitric acid, however, was less efficient than concentration from solutions containing only uranyl nitrate. The feasibility of concentrating uranyl ion by complexing was also demonstrated by tests with the single-membrane assembly; uranyl ion was concentrated from 0.01M uranyl nitrate into 0.2M ammonium oxalate solutions.

Further exploratory tests to find new uses for the membrane separations method showed that strontium can be removed from 0.1M sodium nitrate solutions almost completely by a single batch equilibration with solutions of ethylenediaminetetraacetic acid (EDTA) in which the EDTA concentration is only 0.01M. This result suggests that membrane techniques may be useful to remove ^{90}Sr from waste.

Concentration of Uranyl Ion

Countercurrent Apparatus

~ Baffles?

The countercurrent five-stage concentrator, as sketched in Figure 20, has ten flow compartments separated by nine "AMFion" C103 membranes. The frame around each flow compartment contains 20-mil-thick polyethylene between two 10-mil-thick layers of stainless steel. The frames permit ~2.5 in^2 of each side of each membrane to be exposed to the flowing solutions. Each frame is so cut to ensure that all of the membrane is exposed to the flowing solutions.

The flow channels from stage to stage are so arranged that solution entering at the bottom of one compartment leaves at the top, bypasses the adjacent compartment, and enters at the top of the second compartment. Thus, different solutions flow alternately cocurrent and countercurrent to each other in successive pairs of adjacent compartments.

The countercurrent apparatus was tested for concentrating uranyl ion by pumping a feed solution (0.01M uranyl nitrate) in one direction and a strip solution (3M nitric acid) in the opposite direction through the apparatus. Both flowing solutions were agitated by a pulse pump on the feed stream; the pulsing action was transmitted to the strip solutions by the resultant flexing of the membranes.

Throughout these tests the flow rate of the strip solution was ~0.1 ml/min, and the flow rate of the feed was varied from 1 to 4 ml/min. Test results are shown in the following table. These results are encouraging and demonstrate that countercurrent multistage operation can obtain satisfactory concentration with tolerable losses. Significant improvement can be expected in subsequent tests at higher temperatures and with more efficient membranes, as indicated in the following sections.

Concentration of Uranyl Ion in Countercurrent Membrane Apparatus

Feed composition 0.01M uranyl nitrate
Strip composition 3.0M nitric acid
Temperature 25°C; "AMFion" C103

Flow, ml/min		Uranium			
		Product	Raffinate		
Feed	Strip	M	M	%	Over-all Separation(a)
1	0.085	0.117	5×10^{-6}	0.05	23,000
2	0.12	0.168	4×10^{-5}	0.4	4,100
3	0.13	0.224	4.7×10^{-4}	4.7	4,800
4	0.13	0.281	1.24×10^{-3}	12.4	230

(a) $\frac{\text{Uranium concentration in product}}{\text{Uranium concentration in raffinate}}$

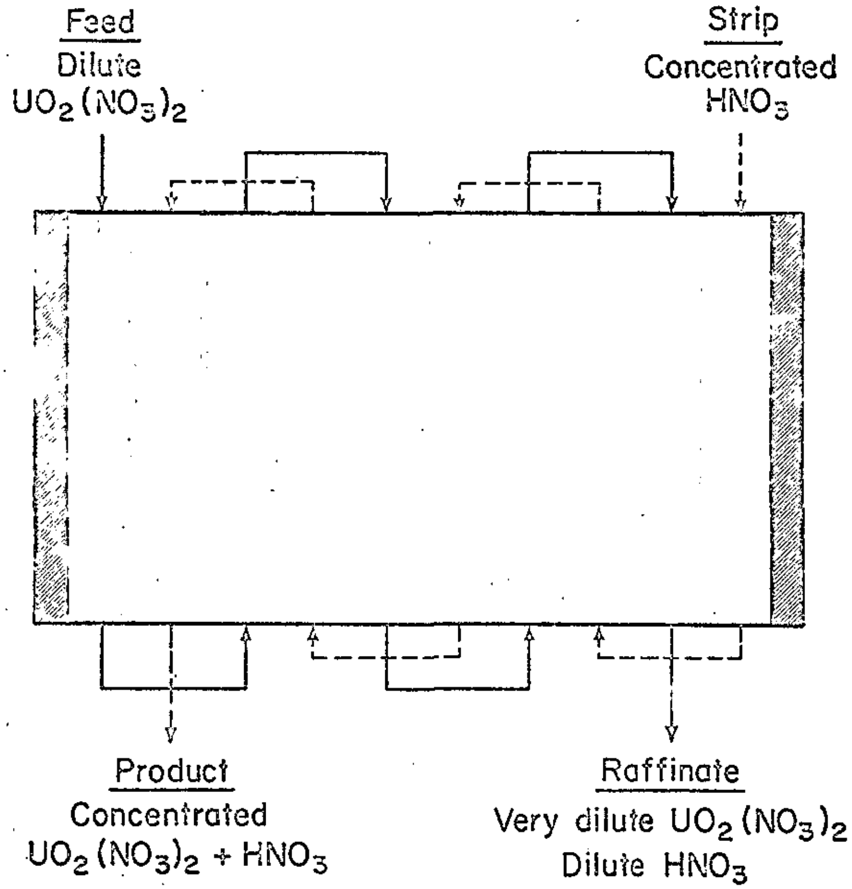

FIG. 20 COUNTERCURRENT FIVE-STAGE CONCENTRATOR

Membrane Efficiency

An apparatus was also constructed that is similar in design to the countercurrent device but contains only one membrane and two flow compartments with transparent end plates. This apparatus was used to determine the relative efficiencies of various types of membrane material, to make preliminary evaluations of process conditions, and to observe the flow patterns within the compartments.

Four different commercial membranes were tested in this device. A feed solution of 0.01M uranyl nitrate and a strip solution of 3M nitric acid were each fed to the apparatus at 0.25 ml/min at room temperature, with pulsing agitation of the feed stream. The product stream (the stream originally containing 3M nitric acid) and the raffinate (the stream originally containing uranyl nitrate) were both analyzed for uranium after ~5-hour flow to reach steady state. An efficiency factor (over-all stage separation) was defined as the product-to-raffinate ratio of the uranium concentrations.

The results of these tests, shown in the following table, demonstrate that "AMFion" C313 is the most efficient of those studied for transferring uranyl ion, and about five times as efficient as "AMFion" C103, which was used for most of the tests with the five-stage concentrator.

Membrane Efficiency Tests

Initial concentrations
  Feed 0.01M uranyl nitrate
  Strip 3M nitric acid
Flow 0.25 ml/min (each stream)
Temperature 25°C

	Uranium Concentration, M		Over-all
Membrane Material	Product	Raffinate	Stage Separation
"AMFion"* C313	1.05×10^{-2}	7.5×10^{-5}	140
"AMFion"* C103	8.0×10^{-3}	3.0×10^{-4}	21
"Ionac"** MC3142	9.4×10^{-3}	1.5×10^{-3}	6.3
"Ionics"*** CR610	7.9×10^{-3}	3.2×10^{-3}	2.5

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***Trademark of Ionics Incorporated.

Effect of HNO_3 in Feed

Several additional tests were made with the one-membrane device, with an "AMFion" C313 membrane to examine the effect of nitric acid in the feed on the concentrating efficiency for uranyl ion. In this series of tests a feed containing 0.01M uranyl nitrate and 0.1M nitric acid was used because it is similar to solutions that will be concentrated in the ^{233}U process; the strip solution was 3M nitric acid. The flow of strip solution was 0.25 ml/min and the flow of the feed solution was varied from 0.25 to 1 ml/min.

The results, shown in the following table, demonstrate that uranyl ion can be concentrated from such a feed but that the efficiency of uranyl transfer is only one tenth of the efficiency for feed containing no nitric acid, with the same membrane. The efficiency was about half that obtained with an "AMFion" C103 membrane when no nitric acid was in the feed.

Although the efficiency is impaired by the presence of acid in the feed, transfer rates of uranyl ion still appear to be large enough to make concentration feasible. Additional details are shown in the following table.

Concentration of Uranyl Ion
from Solutions Containing Nitric Acid
Feed 0.01M uranyl nitrate
0.1M nitric acid
Strip 3M nitric acid

Flow, ml/min		Uranium Concentration, M		
Feed	Strip	Product	Raffinate	Over-all Stage Separation
0.25	0.25	1.14×10^{-2}	7.9×10^{-4}	14.4
0.5	0.25	2.02×10^{-2}	1.72×10^{-3}	11.8
0.75	0.25	2.65×10^{-2}	2.75×10^{-3}	9.7
1.0	0.25	3.0×10^{-2}	3.80×10^{-3}	7.9

Effect of Complexing Agent in Strip Stream

A further series of tests was made with the one-membrane assembly with an "AMFion" C313 membrane, in which 0.2M ammonium oxalate strip was used with 0.01M uranyl nitrate feed.

The results shown in the following table demonstrate that uranyl ion can be concentrated by complexing, but indicate that ammonium oxalate is not an ideal agent to obtain high concentrations. Uranyl oxalate was precipitated when flows were controlled to concentrate the uranyl ion tenfold or more.

Concentration of Uranyl Ion by Complexing with Oxalate
Feed 0.01M uranyl nitrate
Strip 0.2M ammonium oxalate

Flow, ml/min		Uranium Concentration, M		Over-all
Feed	Strip	Product	Raffinate	Stage Separation
0.25	0.25	9.75×10^{-3}	3.19×10^{-4}	31
0.50	0.25	1.8×10^{-2}	9.16×10^{-4}	20
0.75	0.25	2.24×10^{-2}	2.08×10^{-3}	11
0.25	0.025	6.4×10^{-2}(a)	3.56×10^{-4}	--
0.50	0.025	5.54×10^{-2}(a)	1.45×10^{-3}	--

(a) Precipitate formed in apparatus

Removal of Strontium

Batch tests were made to determine the feasibility of removing strontium from sodium nitrate solution by complexing the strontium with EDTA. Such a separation might be useful in removing strontium from process wastes. The tests were made with the equilibration apparatus for the study of membrane equilibrium described in the May 1963 report.

A solution containing 0.1M sodium nitrate and ^{85}Sr tracer was placed on one side of each "AMFion" C103 membrane in the apparatus while a solution containing one of various concentrations of EDTA were placed on the other side of various membranes. Equilibrations were made by revolving the cells for 16 hours, at room temperature. In one series the pH of the EDTA solution was adjusted to 7, and in another series to 10.

The results shown in the following table demonstrate that strontium can be removed from sodium nitrate solution with the membrane separation technique by complexing with EDTA. The removal is more effective at pH 10, as expected, because the concentration of free EDTA ion is greater.

Such batch equilibrium results give no indication of the rate of transfer of strontium across the membranes. Although it is thus not yet possible to say whether a practical process can be designed, the batch measurements do identify which processes are possible and what conditions should be tested in continuous concentrators.

Removal of ^{85}Sr from Sodium Nitrate with EDTA

Feed 0.1M sodium nitrate, ^{85}Sr tracer

EDTA, M	^{85}Sr in Final Solutions, %	
	$NaNO_3$	EDTA
EDTA at pH 7		
0.01	95	5
0.025	76	24
0.05	1	99
0.10	0	100
EDTA at pH 10		
0.025	0	100
0.01	0.2	99.8

Further Tests

Measurements will be made with the nine-membrane concentrator with "AMFion" C313 membranes, which the tests to date have shown to be more efficient. Tests will also be made to develop a method, based on equilibrium across anion exchange membranes, for removing acid from the dilute uranium stream of the ^{233}U process.

ION EXCHANGE MEMBRANE SEPARATIONS

Study was continued of the concentration of uranyl nitrate solutions by Donnan membrane equilibrium. As described in the August and November reports, this technique appears to be quite adaptable to continuous operation, which is a potential advantage over the current method of concentration by ion exchange resin columns in typical B-Line operations.

Equations describing osmotic effects within countercurrent membrane concentrators were derived for use in predicting the operating behavior of the concentrators and defining their limitations and optimum operating conditions. The significance of osmotic transport of water was demonstrated in tests with an eleven-membrane countercurrent concentrator. These tests showed that "AMFion"* C313 cation exchange membrane, contrary to predictions, is less efficient than C103 membrane. The more rapid transport of uranyl ion through the C313 membrane is offset by greater osmotic transport of water.

Description of Osmotic Behavior

Two solutions of different compositions flow in opposite directions through the alternate compartments in the membrane concentrator. Baffles in each compartment route the solutions in such a way that the entire multistage concentrator is equivalent to one long membrane between two narrow compartments. The uranium-stripping solution, ~3M nitric acid, enters at one end of one compartment; and the feed solution, dilute uranyl nitrate, enters at the opposite end of the other compartment.

As the stripping solution progresses along the membrane, uranyl ion is transferred into it by Donnan equilibrium, and water is transferred into it by osmosis. Although the osmotic transport of water is small, the flow of the stripping solution is also small; thus, considerable dilution can occur. This continuous increase in volume of the stripping solution as it progresses through the concentrator reduces the concentration of the acid and increases its rate of flow.

The stripping solution enters the concentrator with f_o nitrate ion content (weight fraction) and with g_o flow (grams/minute). At any distance x from the entry point, the osmosis-affected nitrate content f_x and flow g_x of the stripping solution are functions of x.

The feed solution of uranyl nitrate is so dilute (~0.01M) that its osmotic behavior is essentially that of pure water. The flow of the feed solution is so much faster (~50-100X) than that of the stripping solution that the progressive decrease in feed stream flow and increase in feed stream nitrate concentration caused by osmosis (no nitrate can be transported through the cation exchange membrane) are negligible for the present treatment.

As the stripping solution traverses an element of the long narrow membrane, with width h and length dx, it is diluted osmotically by Φ grams per minute of water from the feed solution, so that its nitrate content decreases from f_x to f_{x+dx}, and its flow changes from g_x to g_{x+dx}. Because the same mass of nitrate must pass every point x

$$f_x g_x = f_o g_o \tag{1}$$

Because the total mass of stripping solution at x+dx is the sum of the mass at x and the mass Φ that enters by osmosis

$$g_{x+dx} = g_x + \Phi \tag{2}$$

or, if ϕ is the osmotic flux per unit area of membrane element (hdx),

$$\frac{dg}{dx} = h\phi \tag{3}$$

The osmotic flux of water per unit area of membrane is assumed to be proportional to the concentration of nitrate in the stripping solution,

$$\phi_x = Bf_x \tag{4}$$

where B = proportionality constant. This assumption is accurate if the rate of osmosis is proportional to the difference in osmotic pressure, and if osmotic pressure is proportional to the difference in concentration. The first of these conditions is normally fulfilled. The second is correct within about ±10% for the solutions of interest; this deviation represents the change in osmotic coefficients of nitric acid between 0.1 and 3M HNO_3.

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Combination of Equations 1, 3, and 4 yields

$$\frac{dg}{dx} = Bh\,\frac{f_o g_o}{g} \qquad (5)$$

Integration from initial flow g_o at $x = 0$ yields

$$\frac{g}{g_o} = \sqrt{1 + \frac{2Bhf_o}{g_o}\,x} \qquad (6)$$

Because the changes in density are relatively small (<10%), the mass flow units for g can be replaced by volume flow units so that the concentrations are expressed as molarity C_o and C. If every membrane in an n-stage concentrator has the same exposed area of membrane $x_s h$,

$$x = nx_s$$

If all constants are combined,

$$\frac{g_n}{g_o} = \frac{C_o}{C_n} = \sqrt{1 + nK\,\frac{C_o}{g_o}} \qquad (7)$$

The constant K is a function of the nature of the membrane, of the exposed area of the membrane, and of the nature but not the concentration of the acid solution.

Tests of Osmotic Behavior

The validity of Equation 7 was tested with an eleven-membrane concentrator with "AMFion" C313 cation membranes. The effects of changes in flow of 0.01M uranyl nitrate feed, and in flow and concentration of the stripping solution were measured. The results are shown in the following table.

The agreement among the values of K indicates the degree of reliability of Equation 7. The values of K are constant within about 13%, which indicates that Equation 7 is useful in predicting the osmotic behavior of countercurrent membrane concentrators.

The concentrations of uranium in the product and raffinate streams illustrate the effectiveness of the "AMFion" C313 membrane assembly. The results, over-all, are not as good as those with "AMFion" C103 that were reported in November. Both the transfer of uranium and that of water are faster with C313. This fact was confirmed by determining K experimentally to be ~0.012 for same system with eleven "AMFion" C103 membranes.

Tests with 11-Stage Concentrator

"AMFion" C313 membrane
Uranyl nitrate feed 0.01M

Stripping and Product Solution					Raffinate
Entrance Flow g_o, ml/min	Exit Flow, g_n, ml/min	Exit Anion Conc C_n, M	Exit U Conc U_n, M	K	Uranium, 0.0001M
C_o = 3M NO_3^-; feed rate g_F 4 ml/min					
0.0843	0.312	0.816	0.140	0.0324	5.8
0.0542	0.233	0.696	0.157	0.0287	8.5
0.0394	0.182	0.652	0.202	0.0242	8.1
C_o = 1M NO_3^-; feed rate g_F 2 ml/min					
0.0954	0.206	0.464	0.0964	0.0313	0.7
0.0615	0.150	0.421	0.132	0.0276	1.0
0.0414	0.110	0.376	0.174	0.0230	3.9
C_o = 0.5M NO_3^-; feed rate g_F 2 ml/min					
0.100	0.158	0.316	0.125	0.0273	1.5
0.595	0.103	0.288	0.143	0.0218	26.0
			Avg	0.0275 ±0.0038	

Attainable Concentration of Uranium

Limits can be placed on the attainable concentrations of uranium, without detailed formulation of the rates of uranium transfer. Solution of the relationships of Equations 7 for C_n in terms of g_n and C_o yields

$$C_n = \frac{C_o}{2g_n}\left(\sqrt{(nKC_o)^2 + 4g_n^2} - nKC_o\right) \qquad (7')$$

Equation 7' is plotted in Figure 32, which shows that C_n approaches C_o asymptotically. Because C_n is the total concentration of nitrate ion in the product stream, the concentration of uranium, U_n, cannot exceed 1/2 C_n. As another limiting condition for U_n, if all of the uranium were extracted by the stripping stream in n stages

$$U_n = \frac{U_F g_F}{g_n}$$

where U_F, g_F = initial values in the feed solution. This equation is also plotted in Figure 32 as a function of g_n.

Because both curves of Figure 32 define upper limits, the concentration of uranium U_n in the product stream is restricted to the shaded region of the figure. The point of intersection of the two curves

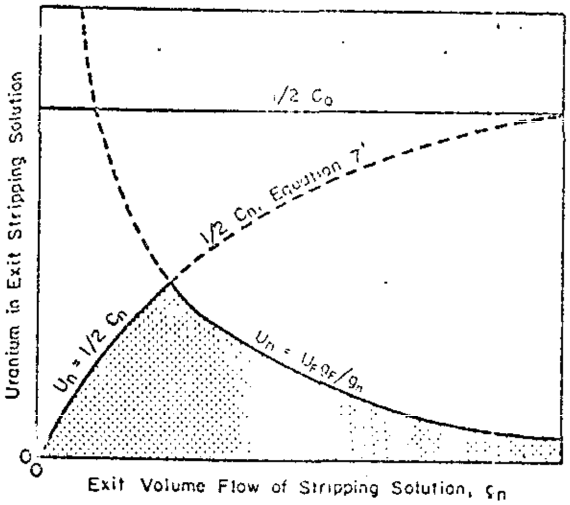

FIG. 32 THEORETICAL CONCENTRATIONS OF UO_2

defines the maximum conceivable concentration of uranium. The condition required at this point is

$$C_n g_n = 2U_F g_F \tag{8}$$

Therefore, by virtue of the identity expressed by Equation 7, the conditions for obtaining the maximum concentration of uranium are controlled by the independent variables C_o and g_o:

$$C_o g_o = 2U_F g_F \tag{9}$$

From Equations 7 and 9, the maximum concentration of uranium is

$$U_{max} = \left[\frac{U_F g_F}{2nK} \bigg/ \left(1 + \frac{2U_F g_F}{nKC_o^2}\right)\right]^{1/2} \tag{10}$$

As C_o approaches infinity, U_{max} approaches $U_{ultimate}$

$$U_{ult} = \sqrt{\frac{U_F g_F}{2nK}} \tag{11}$$

The following conclusions concerning the operation of a membrane uranium concentrator are drawn from the foregoing analysis.

1. The maximum concentration of uranium is obtained when the mole input of stripping nitrate $C_o g_o$ is nearly double that of feed uranium $U_F g_F$. Smaller values of $C_o g_o$ yield lower concentrations and higher

losses; larger values yield lower concentrations and lower losses. The desired operation is with values of $C_o g_o$ as close to $2U_F g_F$ as is consistent with tolerable loss.

2. Higher values of initial nitrate concentration C_o in the stripping solution lead to higher concentrations of uranium in the product, but the advantage is marginal beyond a certain point. When the second term in the denominator of Equation 10 is considerably smaller than unity, a further increase in C_o does not increase U_{max} appreciably. For example, if

the feed concentration U_F is 0.01M,
the feed rate g_F is 2 ml/min,
the strip concentration is 3M NO_3^-,
and nK is 0.30,

the second term would be only 0.015 and U_{max} would be 99.4% of U_{ult}.

3. The ultimate concentration of uranium in the stripping solution and the loss of uranium to the raffinate solution are interrelated closely. Both empirical observations and preliminary theoretical treatments, not included in this report, show that losses to the raffinate decrease with decreasing values of feed flow g_F, but Equation 11 shows that the maximum concentration in the product also decreases with decreasing g_F.

4. An increase in the number of stages n beyond a point may not decrease losses very much. When the number of stages n is increased, in order to maintain the same concentration of uranium in the product the feed flow g_F must also be increased to compensate for the increased osmosis as shown by Equation 11. In the dilute region of the concentrator, however, preliminary calculations of uranium transfer show that the raffinate concentration depends on g_F/n for large n. Thus, an increase of n beyond some minimal value will permit increased throughput for a given raffinate loss, but may not decrease the raffinate loss significantly for a given concentration of uranium in the product.

5. An acid of a divalent anion such as sulfuric acid would probably be a better concentrating agent than nitric acid. The complexing tendency of the sulfate ion for uranyl ions, together with the fact that only one sulfate ion is required per uranyl ion, would permit smaller concentrations of sulfuric acid to effect the desired concentration of uranium. The less concentrated acid would also result in reduced osmosis. Preliminary tests with stripping solutions of sulfuric acid have verified this conclusion.

6. "AMFion" C103 membranes are expected to yield maximum concentrations of uranium about 1.5 times as high as those obtained with C313 membranes at the same rate of flow. This conclusion follows fr Equation 11 and the measured values of K of 0.012 and 0.0275 for the C103 and C313 membranes, respectively.

A new 23-membrane concentrator has been assembled with C103 membranes and is being used to test some of the foregoing conclusions. Theoretical treatment is being developed for the transfer of uranium in the countercurrent assemblies, to provide the basis for more complete descriptions of the characteristics of the concentrators.

The optimum value for α is about 1.5 when nitric acid is used as a stripping agent and provision is made to restrip the uranium in a second concentrator. Smaller values of α lead to increased losses without any significant increase in product concentration; larger values of α lead to smaller concentrations in the product solutions. The optimum value for α when sulfuric acid is used as a stripping solution is $\leqslant 1.2$.

The concentrations of uranium in the product and stripped feed solutions are interdependent. High product concentration is associated with high loss and vice versa. Genuinely optimum conditions of operation do not exist; the proper conditions are obtained by balancing the desired product concentrations with acceptable residual uranium in the stripped solution.

Sulfuric acid is far superior to nitric acid as a stripping solution; both higher product concentrations and lower losses are possible with these solutions. Sulfuric acid, however, is not as compatible with certain possible subsequent processing steps.

Concentration of Uranyl Nitrate in 23-Membrane Separator with Sulfuric Acid

Feed $U_F = 0.01M\ UO_2(NO_3)_2$; (no HNO_3)

Flow, ml/min							H^+, M	
g_F (Feed)	g_o (Strip)	g_p (Product)	α(a)	K(b)	Product UO_2^{2+}, M	Stripped Feed UO_2^{2+}, %	Product	Stripped Feed
Stripping solution $C_o = 1M\ H_2SO_4$								
5.0	0.060	0.144	1.20	0.0124	0.341	1.41	0.101	0.0214
5.0	0.075	0.173	1.50	0.0141	0.289	0.74	0.235	0.0221
5.0	0.200	0.316	4.00	0.0130	0.159	0.62	0.774	0.0233
6.0	0.072	0.169	1.20	0.0145	0.341	3.32	0.166	0.0215
4.0	0.048	0.133	1.20	0.0139	0.276	0.52	0.101	0.0220
3.0	0.036	0.112	1.20	0.0136	0.237	0.11	0.086	0.0224
2.0	0.024	0.0923	1.20	0.0144	0.195	<0.05	0.088	0.0232
Stripping solution $C_o = 2M\ H_2SO_4$								
10	0.060	0.191	1.20	0.0119	0.451	9.83	0.266	0.0215
9	0.054	0.177	1.20	0.0115	0.463	7.45	0.226	0.0215
8	0.048	0.166	1.20	0.0114	0.448	7.62	0.194	0.0218
7	0.042	0.155	1.20	0.0115	0.420	3.94	0.152	0.0218
6	0.036	0.134	1.20	0.0100	0.405	3.56	0.081	0.0205

(a) $\alpha = C_o g_o / U_F g_F$

(b) K defined as in preceding table

Recycle System for Donnan Dialysis

Although higher concentrations of uranium in the product stream are associated with larger concentrations of residual uranium in the stripped feed stream when a single concentrator is used, high concentration in the product and nearly complete stripping can be obtained with two concentrators in series. The first concentrator is operated (with α close to unity) to obtain high concentration of uranium in the product. The stripped feed, which contains considerable residual uranium, flows into a second concentrator, which is operated (with α at a very high value) to strip the uranium nearly completely. The product stream from the second concentrator contains uranium at approximately the same concentration as that of the initial process feed stream; this product is blended with the feed stream to the first concentrator.

A series of tests was completed with two 23-membrane concentrators in series. The first concentrator was fitted with "AMFion" C103 membranes and the second with "AMFion" C313 membranes. The C313 membrane material was used in the second concentrator because tests described in the March report demonstrated that C313 transports uranium more rapidly than C103. Although C313 also transports water more rapidly, this is relatively unimportant in the second concentrator because high concentrations of uranium are not necessary in the second product (recycle) stream.

The feed to the first concentrator was 0.01M uranyl nitrate as in the previous tests; the stripping solution for the first concentrator was 2M sulfuric acid and that for the second concentrator was 2M nitric acid. Feed flows of 10, 7.5, and 5.0 ml/min were used in three tests; the flow of stripping solution to the first concentrator was adjusted to maintain constant $\alpha = 1.2$. The flow of stripping solution to the second concentrator was 0.12, 0.10, and 0.06 ml/min, respectively, for the initial feed rates of 10, 7.5, and 5.0 ml/min.

The results of these experiments are summarized in the following table. The data show that uranium can be stripped almost completely and at the same time concentrated to ~0.45M (107 g/liter). The uranium in the raffinate in the two tests with the low flow is well below 0.1%, which is usually an acceptable loss. The loss is expected to be reduced further, without reducing the product concentration, by increasing the size of the second separator. The product concentration for the tests at feed rates of 10 and 7.5 ml/min are quite consistent with data reported previously. The product concentration for the test at feed rate = 5 ml/min was less than expected, probably due to a malfunction of the pump for the stripping solution -- the flow of the product stream was higher than expected.

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Although the foregoing tests were made with sulfuric acid in the first stripping solution, the same procedure can be used with nitric acid as the initial stripping solution. On the basis of the results summarized in the preceding section, concentration of 0.01M uranium solutions to ~0.27M (64 g/l) appears to be practicable, with recycle of ~3% of the uranium.

Concentration of UO_2^{2+} in Recycle Donnan Dialysis System

Feed 0.01M $UO_2(NO_3)_2$

Stripping solutions
First concentrator 2M H_2SO_4
Second concentrator 2M HNO_3

Feed Flow, ml/min	UO_2^{2+}, M		UO_2, % of initial feed		
	Product	Recycle(a)	Product	Recycle(a)	Raffinate(b)
10	0.472	0.024	89	10.4	0.35
7.5	0.436	0.0092	95	5.0	0.044
5.0	0.338	0.0032	98	1.7	0.014

(a) Product from second concentrator
(b) Stripped feed from second concentrator

De-acidification Donnan Dialysis with Anion Exchange Membranes

The tests that have been summarized in the preceding sections and in previous reports have involved the concentration of dilute solutions of pure uranyl nitrate. However, the recycle stream and the initial feed in many actual processes will contain fairly high concentrations of nitric acid. Tests and theoretical considerations indicate that nitric acid in significant concentrations decreases the efficiency of the membrane concentrator (as with other cation exchange processes), and simple neutralization of the excess acid with an alkaline solution is not a suitable remedy because the added cation also interferes.

Preliminary tests have shown, however, that the acid can be neutralized by anion exchange membrane dialysis without the addition of extraneous cations. De-acidification separators are otherwise identical in design to the concentrators used in the foregoing tests. The feed solution containing excess nitric acid is fed into compartments on one side of the membranes and a solution of sodium hydroxide is fed into the compartments on the opposite side of the membranes. The nitrate and hydroxide ions are exchanged; the sodium and uranyl ions are not. The exchanged hydroxide ions neutralize the hydrogen ions in the feed solution.

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Complete Concentration System

The complete system for concentration of uranium will contain three membrane separators, one for de-acidification, one for concentration, and one for recycle as shown in Figure 12. The compositions of the solutions shown in the figure represent one of several systems that can be used.

Tests are being made to develop the de-acidification step and the complete dialysis system more completely. Tests are also in progress to demonstrate the concentration of other ions, such as Sr^{2+} from $NaNO_3$ solutions and La^{3+} from dilute solutions. A center-feed separator is being constructed for tests of the separation of two ions such as Cu^{2+} and Ag^+, preliminary to tests with curium and americium.

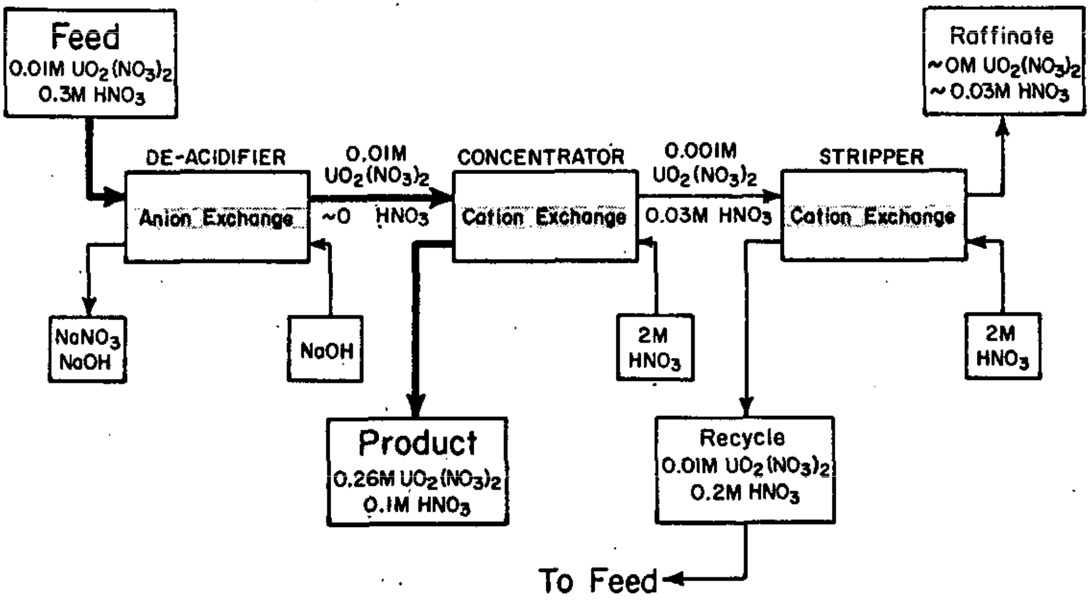

FIG. 12 COMPLETE DONNAN DIALYSIS CONCENTRATION SYSTEM FOR UO_2^{2+}

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ION EXCHANGE MEMBRANE SEPARATIONS

Further tests confirmed that solutions of uranyl nitrate are concentrated in excellent yield by the three stages of ion exchange dialysis described in the June report. The dialysis technique -- based on approach to Donnan equilibrium across ion exchange membranes -- is readily adaptable to continuous operation and therefore offers a distinct advantage over the present plant processes for batchwise concentration with columns of ion exchange resin.

Other tests confirmed the expectations that the membrane techniques for concentrating divalent UO_2^{2+} are equally effective for concentrating trivalent ions such as Pu^{3+}, and that they should be useful for removing strontium from waste streams.

Concentration of UO_2^{2+}

Figure 24 shows the over-all ion exchange process for concentrating uranyl nitrate. Three steps of dialysis are used:

> The anion exchange deacidifier in the first step removes excess H^+ from the feed; high acidity would limit the concentration of UO_2^{2+} that can be obtained in the second step.
>
> The cation exchange concentrator in the second step provides the desired increase in concentration of UO_2^{2+}.
>
> The cation exchange concentrator in the third step strips the residual UO_2^{2+} from the raffinate, at suitable concentrations for blending with the feed stream.

Each stage is a series of compartments separated by the ion exchange membrane. The two influent solutions flow in opposite directions through alternate compartments (Figure 25), and baffles in each compartment direct the flow in such a way that the over-all assembly is equivalent to a very long membrane between two very narrow compartments. Tests of the two cation exchange concentrators were summarized in the June report, but only preliminary results were described for the anion exchange deacidifier.

[redacted]

[redacted]

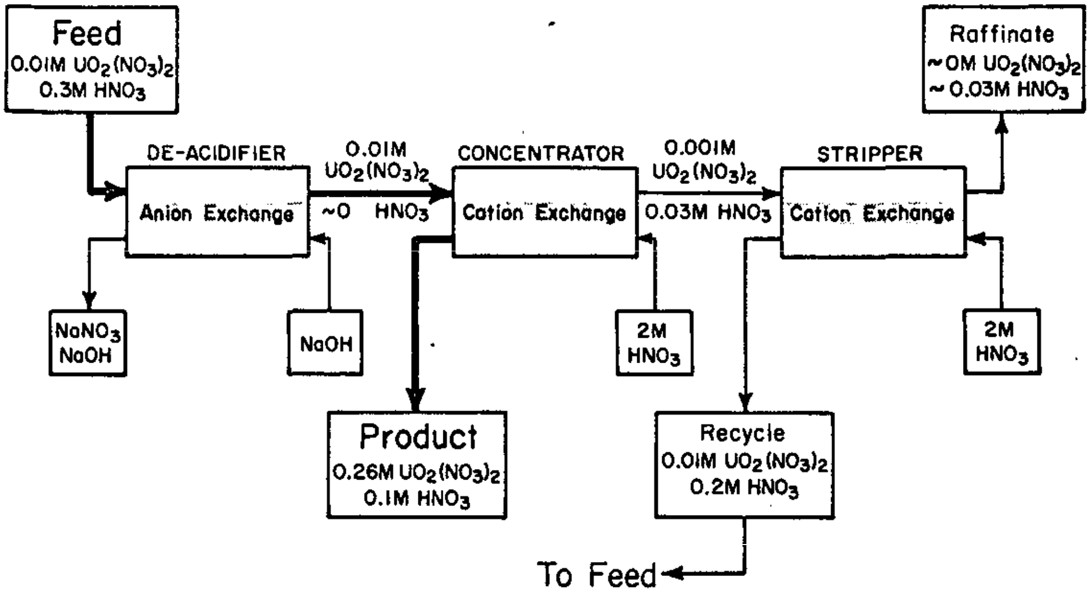

FIG. 24 COMPLETE DONNAN DIALYSIS CONCENTRATION SYSTEM FOR UO_2^{2+}

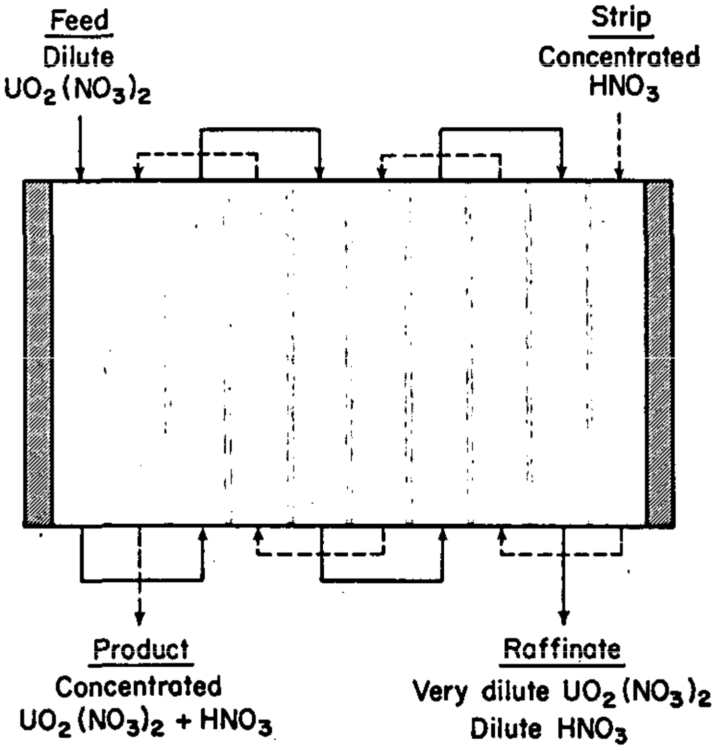

FIG. 25 MEMBRANE DIALYSIS CONCENTRATOR

[redacted]

Subsequent tests with the deacidifier have demonstrated that the concentration of HNO_3 in typical feed (0.01M UO_2^{2+}, 0.3M HNO_3) can be reduced to any desired value, with only ~0.1% loss of uranium to the NaOH solution. About 3 liters of synthetic feed was deacidified to pH 3.8 (approximately the pH of unacidified 0.01M uranyl nitrate), and then processed through the two concentrators to demonstrate the complete system. The product contained 0.27M UO_2^{2+}. Only 0.1% of the UO_2^{2+} remained in the raffinate. The UO_2^{2+} in the raffinate could be reduced still further by minor changes in process conditions. The only apparent defect in the system is a relatively high content of Na^+ in the product, due to slight permeation of Na^+ through the anion exchanger in the deacidifier and subsequent concentration by cation exchange along with the UO_2^{2+}.

Anion Exchange Deacidification

The dialysis deacidifier has the same construction as the cation concentrators. The feed solution containing excess nitric acid flows through the compartments on one side of the anion exchange membrane and a solution of sodium hydroxide flows through the compartments on the opposite side; both of the flowing solutions are agitated by pulsing. The NO_3^- and OH^- are exchanged but the Na^+ and UO_2^{2+} are not. The exchanged OH^- neutralizes the H^+ in the feed solution.

A feed solution containing 0.01M $UO_2(NO_3)_2$ and 0.3M HNO_3 was used in a series of tests with an 18-compartment deacidifier with "AMFion"* A104 membrane. The concentration of the NaOH solution was varied between 1 and 1.5M, and the acidity of the product stream was controlled by adjusting the flows of the feed and NaOH.

Although no attempt was made to optimize operating conditions for the deacidifier, sufficient work was done to demonstrate that:

> The effluent UO_2^{2+} solution can be controlled at any pH between 1 and 5.5 by adjusting the flows of the two streams.
>
> Uranium oxide is precipitated when the pH of the feed solution reaches 5.5, but is dissolved rapidly when the acidity is increased by slight increase in flow of the feed.

Permeation of UO_2^{2+} through the anion exchange membrane to the spent NaOH was very small; the maximum observed UO_2^{2+} in this stream was about 5×10^{-6}M. However, appreciable Na^+ permeated the membrane into the UO_2^{2+} stream; although the maximum observed concentration of 0.005M is small compared with that of the initial 0.3M H^+, it is half the concentration of the UO_2^{2+}. The data are summarized in the following table.

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Deacidification of Uranyl Nitrate Solution

Dialyzer 24-compartment anion exchanger
Feed 0.01M $UO_2(NO_3)_2$ - 0.30M HNO_3
Nitrate strip 1.5M NaOH

Flow, ml/min		Deacidified Feed		UO_2^{2+} in Spent NaOH,
Feed	NaOH	pH	Na^+, 10^{-3}M	10^{-6}M
2.75	3	1.12	5.91	3.0
2.75	4	1.43	5.67	5.1
2.75	6.5	3.83	5.56	3.0
2.75	7.5	4.18	5.73	4.1

Test of Complete System for Concentrating UO_2^{2+}

The complete system for concentrating UO_2^{2+} was tested with a 3-liter batch of synthetic feed containing 0.3M HNO_3 and 0.01M $UO_2(NO_3)_2$. The test demonstrated that the deacidifier effluent is suitable feed for the concentrators.

The feed was first processed through the 18-compartment anion exchange deacidifier alone, and was then processed through the two cation exchange concentrators in series. The flow of feed to the deacidifier was 2.7 ml/min and the flow of 1.5M NaOH was 6 ml/min. Both streams were agitated by pulse pumps. The effluent contained 0.010M UO_2^{2+} and 0.0056M Na^+ at pH 3.82.

The batch of effluent solution from the deacidifier was fed to the two concentrators (24 compartments each) at 5.13 ml/min; 2.0M HNO_3 stripping solution was fed to the first concentrator at 0.075 ml/min and to the second concentrator at 0.060 ml/min. The results are summarized in the following table.

Concentration of Uranium from Deacidified Feed

	Flow, ml/min	UO_2^{2+}, 10^{-3}M	H^+, M	Na^+, 10^{-3}M
Product	0.189	270	0.131	86.5
Recycle	0.230	26.3	0.208	15.3
Raffinate	5.13	0.01	0.040	1.6

[redacted]

The concentration of UO_2^{2+} in the product, >60 g/l, was almost identical to that obtained in previous tests with unacidified solutions of uranyl nitrate. The UO_2^{2+} in the final stream for recycle (~10%) and the UO_2^{2+} in the final raffinate (0.1%) were slightly higher than in previous tests. These values can be reduced with small adjustments in process control.

The only potentially serious problem is the relatively high concentration of Na^+ in the product (nearly 0.1M). The Na^+/UO_2^{2+} concentration ratio in the product is ~1/3 -- although this is less than the ratio of 1/2 in the feed to the cation concentrators (because of poorer efficiency in concentrating the monovalent Na^+) it is sufficiently large to be of concern. The Na^+ might be coprecipitated when the uranium is precipitated as ammonium diuranate. If such is the case, ammonium hydroxide or perhaps a quaternary alkyl ammonium hydroxide may be preferred as neutralizing solutions in the deacidifier. This problem will be investigated in future tests.

Larger dialysis equipment is being developed for further tests of the over-all UO_2^{2+} concentration process.

Concentration of Tripositive Ions

Tests with La^{3+} demonstrated the effectiveness of membrane dialyzers in concentrating trivalent ions. La^{3+} was concentrated from a dilute solution of $La(NO_3)_3$ with HNO_3 stripping solution, almost as efficiently as UO_2^{2+}. Thus, Pu^{3+} can probably be concentrated by dialysis from dilute plant streams by nearly the same conditions as those developed for UO_2^{2+}. Thermodynamically, the trivalent cations should be concentrated more efficiently than divalent cations, but this effect is opposed by slower rate of transport of the trivalent ions through the membrane. Further tests demonstrated that lanthanum can also be concentrated by complexing with ethylenediaminetetraacetic acid (EDTA).

The tests with HNO_3 stripping solutions were made with one 24-compartment concentrator. The data are summarized in the following table. Each test was made with a 50% stoichiometric excess of influent strip NO_3^- relative to influent feed La^{3+}. The concentration of lanthanum in the products was very nearly the same as that obtained for uranium under the same conditions. Residual La^{3+} in the raffinates was slightly higher than for UO_2^{2+} under the same conditions; these data indicate that the rate of transfer of the tripositive ions is somewhat slower than that of dipositive ions. The La^{3+} in the raffinate from the single concentrator is sufficiently low, however, that lanthanum (and therefore probably plutonium) could be concentrated adequately and recovered completely if the over-all system of Figure 24 were used.

Concentration of La^{3+} with Nitric Acid

Feed 0.0103M $La(NO_3)_3$
Strip 2.02M HNO_3

Flow, ml/min			La^{3+}, 10^{-3}M		H^+, 10^{-3}M	
Feed	Strip	Product	Product	Raffinate	Product	Raffinate
5	0.112	0.185	262	1.19	198	39.2
3	0.067	0.113	257	0.89	49	43.5

In another series of tests with one 24-compartment concentrator, the La^{3+} was concentrated with a stripping solution of 0.1M EDTA buffered to pH 7. These experiments demonstrated that trivalent ions can be concentrated with a fairly dilute solution of a powerful complexing agent. As shown in the following table, the La^{3+} was transferred nearly quantitatively into the EDTA solution when the flow of the feed was sufficiently slow. The residual La^{3+} in the raffinate, however, increased rapidly when the flow exceeded 2 ml/min. No attempt was made to obtain product solutions of very high concentrations because of the limited solubility of EDTA.

Study of the concentration of trivalent cations will be continued after a pilot-scale demonstration of the concentration of UO_2^{2+} is completed.

Concentration of La^{3+} with EDTA

Feed 0.0103M $La(NO_3)_3$
Strip 0.1M EDTA (pH 7)

Flow, ml/min		La^{3+}, 10^{-3}M	
Feed	Strip	Product[(a)]	Raffinate
2.00	0.500	40	0.018
3.00	1.0	30	0.165
4.0	1.0	30	1.05

(a) Calculated by mass balance

Removal of Strontium from Solutions of Sodium Nitrate

Tests with batch apparatus for membrane dialysis that were summarized in the November 1964 report demonstrated that Sr^{2+} is removed completely from a 0.1M $NaNO_3$ solution by complexing with EDTA buffered to pH 10. This separation has now been demonstrated with continuous dialysis.

A solution containing 0.10M $NaNO_3$ and 0.00119M $Sr(NO_3)_2$ was fed at 2 ml/min through two 24-compartment concentrators in the series arrangement of Figure 24. A stripping solution of 0.04M EDTA buffered to pH 10 was fed through each of the concentrators at 0.10 ml/min -- the concentration of 0.04M EDTA is approximately iso-osmotic with 0.1M $NaNO_3$. The two stripping solutions were kept separate only for analytical accuracy in evaluating performance. The Sr^{2+} in the effluent from the first separator was near the limit of detection; hence the second separator was required to concentrate the residual strontium (by ~20) to enable a reliable estimate of the decontamination factor across the first dialyzer.

The tests are summarized in the following table. Virtually all of the strontium, concentrated 20-fold, was recovered in Product 1; much larger concentration factors can be obtained with higher concentrations of EDTA in the strip (or with more dilute strontium feed solutions). In the present test the effluent EDTA was approximately half-saturated with strontium. The decontamination factor was 4300 for removal of strontium from sodium nitrate in the first separator. The strontium in the final raffinate was too low to be detected, but the data for the first separator indicate that the over-all decontamination factor for the two dialyzers is probably ~10^7.

This test indicates that Donnan dialysis should be effective for recovering strontium or for decontaminating certain waste streams. Study of the removal of strontium will be resumed when specific applications are needed.

Removal of Strontium from Sodium Nitrate with EDTA

Feed 1.19×10^{-3}M $Sr(NO_3)_2$, 0.10M $NaNO_3$
Strips 1 and 2 0.04M EDTA (pH 10)

	Flow, ml/min	Sr^{2+}, M
Feed	2.0	1.19×10^{-3}
Strip 1	0.10	-
Strip 2	0.10	-
Product 1	0.10	2.28×10^{-2}
Product 2	0.10	5.6×10^{-6}
Raffinate 1	2.0	2.8×10^{-7}(a)
Raffinate 2	2.0	Not detectable

(a) Estimated from the concentration of Sr^{2+} in Product 2 and the flow rates.

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ION EXCHANGE MEMBRANE SEPARATIONS

Separation of Silver and Copper

Continuous processing by ion exchange dialysis was extended in the laboratory to demonstrate the separation of silver from copper, preliminary to planned separations of two ions, such as curium from americium. The continuous dialysis, which is based on approach to Donnan equilibrium across ion exchange membranes, was shown previously to be useful for concentrating ionic species such as UO_2^{2+} and La^{3+}, and for removing cationic nuclides such as radiostrontium from simulated radioactive waste solutions (October report, page 82).

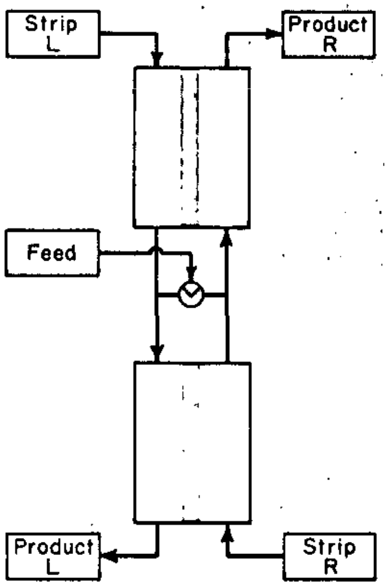

FIG. 23 CENTER-FED CATION EXCHANGE DIALYSIS

The tests with Ag^+ and Cu^{2+} were made with a center-fed dialysis system comprising two 24-compartment separators containing "AMFion"* C103 membranes (Figure 23). As in the separators described in the October and June reports, the two influent solutions flow in opposite directions through alternate compartments in each separator, and baffles in each compartment direct the flow in such a way that the over-all separator is equivalent to a very long continuous membrane between two very narrow compartments.

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The feed solution containing the ions to be separated was blended with one or the other of the flowing solutions, at a point between the two separators. All streams were fed with metering pumps, and the two stripping solutions were pulsed to provide agitation. A mixed solution of silver and copper ions was chosen for the initial tests of cationic separation because these ions are amenable to separations based on either the difference in their charges or differences in stability among a variety of their complexes.

Four different processes were studied; all were successful to some extent:

1. Separation based on the difference in charge of the Ag^+ and Cu^{2+} ions, in which nitric acid of different concentrations was used as the separating medium, was the least successful; in the best case, equimolar silver and copper in the feed were separated into two fractions -- one contained 68% silver and 32% copper, the other contained 90% copper and 10% silver.

2. Separation based on preferential complexing of copper by ethylenediaminetetraacetic acid (EDTA) or by diethylenetriaminepentaacetic acid (DTPA) -- in which a solution of sodium nitrate was used as the silver stripping solution and the feed was added to this solution between the separators -- gave consistently a copper product containing no detectable silver and a silver product with 0.3 to 9 mole % copper.

3. Separation similar to 2, but in which the feed was introduced into the DTPA copper stripping solution, demonstrated much larger capacity than Method 2 and consistently yielded products containing <2 mole % of the other component.

4. The best over-all results were obtained by separation similar to 3 but with sodium thiosulfate as a complexing agent in the silver stripping solution. This method had the same capacity as Method 3, yielded a silver product that was more concentrated than that of any other method, and none of the products contained >0.15 mole % of the other component.

Separation Based on Difference in Charge (Method 1)

Separation of cations of different charges depends on preferential concentration of the cations of higher charge into the more concentrated of two solutions separated by the cation-permeable membrane. If the two solutions contain nitric acid at different concentrations, for example, and small amounts of Ag^+ and Cu^{2+} are introduced, both ions will be concentrated in the more concentrated solution of acid, but Cu^{2+} will be concentrated to a greater extent than Ag^+. The two ions are separated in the center-fed membrane system by adjusting the flows

[redacted]

of the streams so that relatively more silver is transported in the dilute acid stream at high flow and more copper is transported in the opposite direction by the concentrated acid stream at low flow. The conditions for such operation of such a system are derived as follows.

A cation of charge z^+ is distributed as follows between two acid solutions of different concentrations, separated by a cation-permeable membrane:

$$\frac{C_R^{z+}}{C_L^{z+}} = \left(\frac{H_R}{H_L}\right)^z \tag{1}$$

where C^{z+}, H = respective activities (approximately the concentrations) of the cation and hydrogen ion

R, L = opposite sides of the membrane

In a single stage at equilibrium in which Solutions R and L flow in opposite directions at rates g_R and g_L ml/min, respectively, the number of moles of cation transported from the stage per unit time is $C_R^{z+}g_R$ plus $C_L^{z+}g_L$. An extraction factor E_L^R may then be defined:

$$E_L^R = \frac{C_R^{z+}g_R}{C_L^{z+}g_L} \tag{2}$$

or from Equation 1

$$E_L^R = \left(\frac{H_R}{H_L}\right)^z \frac{g_R}{g_L} \tag{3}$$

If two ions of different charge z_A and z_B are to be separated, the greatest resolution will be obtained when

$$\left(E_L^R\right)_A = 1/\left(E_L^R\right)_B \tag{4}$$

Combination of Equation 3, with values of z for each ion, with Equation 4 yields the flow rates that satisfy Equation 4:

$$\frac{g_R}{g_L} = \left(\frac{H_R}{H_L}\right)^{-\frac{(z_A + z_B)}{2}} \tag{5}$$

[redacted]

In the tests with silver and copper, 1M HNO_3 was the concentrated solution (Strip R) and 0.25M HNO_3 was the dilute solution (Strip L). Use of these values for H and the charges $z_A = 1$ and $z_B = 2$ in Equation 5 yields a value of 8 for the flow ratio, that is, the more dilute stream must flow eight times as fast as the concentrated stream. The respective extraction factors E_L^R for silver and copper are found from Equation 3 to be 2 and 0.5. In practice the same flow ratio cannot be used in both separators because the feed stream contributes to the flow in the second separator only. This effect was minimized by introducing the feed at slow flow into the rapidly moving dilute (Strip L) stream. The flow ratios were varied from 7.6 to 8.2.

The results of the two tests listed in the following table show that cations can be separated from each other on the basis of differences in charge. Equimolar amounts of copper and silver in the feed were separated into two fractions, one enriched in copper and the other enriched in silver. The failure of the system to effect more complete separation was due to the relatively small driving force of the process and the slow rate of ion exchange through the membranes. The efficiency of this separation might be improved, but much more efficient separations are possible by the use of complexing agents, as described in the following sections.

Separation of Silver from Copper Based on Ionic Charge

Feed L 0.1M $Cu(NO_3)_2$, 0.1M $AgNO_3$
Strip R 1.0M HNO_3
Strip L 0.25M HNO_3

Flow, ml/min			Ag Product L			Cu Product R		
			Molarity	Mole %		Molarity	Mole %	
Feed	Strip R	Strip L	Ag + Cu	Ag	Cu	Ag + Cu	Ag	Cu
0.15	0.2	1.5	0.0218	68	32	0.0262	10	90
0.3	0.4	3.0	0.0181	64	36	0.0435	13	87

Separations Based on Complexing (Methods 2,3,4)

Separations based on complexing depend on preferential concentration of an ion in one of two solutions separated by an ion-selective membrane when the concentrating solution contains a compound that reacts with the ion to form a complex. The conditions under which separation is obtained are formulated as follows for the equilibrium distribution of a single cationic species C between two solutions R and L separated by a cation-permeable membrane. In the most general case, each of the two solutions will contain a complexing agent -- Y_R in solution R, and Y_L in solution L -- the two agents may or may not be the same. The solutions also contain acids or salts with univalent cations. These univalent cations may be associated either with the complex-forming anions Y or other noncomplexing anions; their concentrations are M_R and M_L.

Cation C^{z+} reacts with complexing agent Y in one of these solutions:

$$C^{z+} + Y \rightarrow CY$$

The equilibrium constant for the reaction is

$$K = \frac{(CY)}{(C^{z+})Y} \tag{6}$$

The total concentration (C) of the species is the sum of the complexed (CY) and uncomplexed (C^{z+}) portions

$$(C) = (C^{z+}) + (CY) \tag{7}$$

The combination of Equations 6 and 7 yields

$$(C) = (C^{z+})(1 + KY) \tag{8}$$

An Equation 8 can be written for each solution R and L. The ratio of the two equations is

$$\frac{(C_R)}{(C_L)} = \frac{(C_R^{z+})}{(C_L^{z+})} \frac{(1 + K_R Y_R)}{(1 + K_L Y_L)} \tag{9}$$

where C_R, C_L = total complexed and noncomplexed element in solutions R and L

C_R^{z+}, C_L^{z+} = concentrations of uncomplexed ions

Y_R, Y_L = concentrations of complexing agents

K_R, K_L = equilibrium constants for the complexing reaction

Because Donnan membrane equilibrium exists, Equation 1 must also be satisfied. Combination of Equations 1 and 9 yields

$$\frac{(C_R)}{(C_L)} = \left(\frac{M_R}{M_L}\right)^z \frac{(1 + K_R Y_R)}{(1 + K_L Y_L)} \tag{10}$$

Equation 10 defines the distribution coefficient D_L^R of the cation between the two solutions. If the two solutions are flowing through the system with flows g_R and g_L, and the distribution of the cation is always at equilibrium, the system can be treated mathematically as a single extraction stage. The extraction factor E_L^R is obtained by multiplying Equation 10 by the flow ratio g_R/g_L:

$$E_L^R = \frac{g_R}{g_L}\left(\frac{M_R}{M_L}\right)^z \frac{(1 + K_R Y_R)}{(1 + K_L Y_L)} \qquad (11)$$

Equation 11 applies to each ion, although different extraction factors will be obtained because of differences in K_R and K_L.

To separate two ions, one extraction factor must be greater than unity and the other less than unity. If a specific complexing agent can be found for each ion, then K_R will be large and K_L small for one ion, and the reverse for the other. The separation can then be obtained by suitable adjustment of the concentrations of Y_R and Y_L. Although such convenient complexing agents are not normally available, separation can still be obtained if one ion is complexed and the other is not. The third factor on the right side of Equation 11 will then be large for one of the ions, but unity for the other. The extraction factor of the second ion can be decreased by reducing the product of the first and second terms -- by increasing the salt or acid in the solution without the complexing agent, and by increasing the flow of the noncomplexing stream above that of the complexing stream.

Most of the common complexing agents are not extremely specific. For effective separation, the product KY in one solution must be large for one ion and small for the other. This condition can be obtained by adjusting the effective concentration of the complexing agent Y. Because most complexing agents are salts of weak acids, this adjustment is most effectively obtained by adjusting the pH of solutions that contain a fairly large gross concentration of the agent -- and hence a large separation capacity. In some instances, where the two ions to be separated both have very large stability constants with the complexing agent, adjustment of the pH of the solutions may be impractical because the high concentration of acid required for proper adjustment of Y will cause precipitation of the acid forms of the complexing agents. In these cases the adjustment may conceivably be obtained by introducing a third cation whose stability constant is between those of the two ions to be separated.

The following summary of the separation of silver and copper illustrates some of the foregoing aspects. The stability constant of Cu·EDTA is approximately 10^{18} while that for Ag·EDTA is only 10^{7}. The pH of a solution of 0.01M Na_2H_2EDTA is ~5, from which the concentration of free EDTA anion can be calculated to be about 5×10^{-9} based on published dissociation constants of the acid. The value of K_RY_R for copper is therefore 5×10^9 and that for silver is 5×10^{-2}. When the EDTA is in Solution R, the respective values of $(1 + K_RY_R)$ for copper and silver are therefore $\sim 5 \times 10^9$ and ~ 1. At pH 5, the EDTA solution contains primarily Na^+ ions and $H_2EDTA^=$ ions; hence the concentration of Na^+ ions in a 0.01M solution of the EDTA is ~0.02M. If Solution L contains 0.1M $NaNO_3$, the M_R/M_L ratio (in this case Na_R/Na_L) in Equation 11 is 0.2. Because neither copper nor silver is complexed by nitrate ion, $K_L = 0$ for both ions. If the flow ratio g_R/g_L is unity, the respective factors E_L^R for silver and copper are 0.2 and 2×10^8; silver will be concentrated in the L stream and copper will be concentrated in the R stream, so that a suitably large center-fed dialysis separator can separate the ions almost completely.

In practice, the extraction factor for silver is probably <<0.2 in the part of the system that is most concentrated in copper, because the exchange of copper for sodium ions across the membrane is followed by a reaction of the copper with the $H_2EDTA^=$ ions to form $CuEDTA^=$ and $2H^+$. The hydrogen ions, however, are removed by reaction with excess $H_2EDTA^=$ to form H_3EDTA^-, thus reducing the total cation concentration in the solution.

Introduction of Feed in Noncomplexing Stream (Method 2)

The foregoing separation was tested in a center-fed dialysis system. A feed solution containing 0.1M $AgNO_3$ and 0.1M $Cu(NO_3)_2$ was fed into noncomplexing Strip L between the two separators. The noncomplexing Strip L, which contained 0.1M $NaNO_3$, was fed into one end of the system; and a complexing strip stream of 0.01M Na_2H_2EDTA (Strip R) was fed into the other end at a rate designed to maintain an excess of 20% EDTA over that necessary to complex the copper. The results of these tests are shown in the following table. The copper product streams (R) contained no detectable silver; the silver streams (L) contained small but significant amounts of copper, which increased with increasing flow -- all of the copper must pass through the membrane to concentrate in the EDTA stream, but the bulk of the silver simply remains in the noncomplexing stream. The copper content of the silver stream should be decreased by reducing the flow of the feed and noncomplexing streams.

One difficulty with EDTA in dialysis separations is the very low solubility of the acid H_4EDTA, which limits the conditions of use. In some preliminary tests, the reaction of copper with EDTA liberated so much hydrogen ion that H_4EDTA was precipitated in the membrane separator. Tests therefore were made also with the more soluble DTPA as the complexing agent. Although data on the stability constant of the silver complex are not available, estimates based on the behavior of silver with other complexing agents suggested that at pH 4, no silver complex would form, while the copper ion would be complexed extensively. The best separation was obtained when the flow of the complexing stream was adjusted to give a 50% excess of DTPA over the copper; the copper stream was free of detectable silver and the silver stream contained only 0.3 mole % of copper.

The tests with both complexing agents demonstrated quite clearly that relatively clean separation of ions are obtained by Donnan dialysis. Significant improvements in the process can probably be made with further development.

Separation of Silver and Copper by Complexing

Feed added to noncomplexing solution
B Feed (L) 0.1M $Cu(NO_3)_2$, 0.1M $AgNO_3$
B Noncomplexing Strip L 0.1M $NaNO_3$

	Flow, ml/min		Ag Product L B		Cu Product R A	
Feed	Noncomplexing L B	Complexing R A	Molarity Ag + Cu	Cu, mole %	Molarity Ag + Cu	Ag, mole %
Complexing Stream 0.01M EDTA (pH 5)						
0.1	1.0	1.2	7.66×10^{-3}	2.7	8.0×10^{-3}	<0.025
0.2	2.0	2.4	1.12×10^{-2}	9.1	4.0×10^{-3}	<0.05
Complexing Stream 0.01M DTPA (pH 4)						
0.1	2.0	1.2	4.92×10^{-3}	2.5	9.4×10^{-3}	<0.025
0.1	1.0	1.2	9.3×10^{-3}	3.2	9.0×10^{-3}	<0.025
0.1	1.0	1.5	8.9×10^{-3}	0.3	5.9×10^{-3}	<0.03

Introduction of Feed in Complexing Stream (Method 3)

Introducing the feed into the complexing stream, rather than into the noncomplexing stream as described in the preceding section, has advantages in some cases. In separating silver and copper, feeding to the complexing stream forces exchange transport of the more mobile Ag^+ cation (rather than the Cu^{2+} cation) and simultaneously causes the Ag^+ to be transported from a dilute into a concentrated stream, which is advantageous kinetically. Introduction of the feed into the stream containing the copper complexing agent also permits the use of a different complexing agent for silver in the opposite stream.

In the first tests of this type, the feed of 0.1M $AgNO_3$ and 0.1M $Cu(NO_3)_2$ was introduced at the center of the system into a solution (Strip R) that contained 0.05M DTPA adjusted to pH 7. The opposing Strip L contained 0.3M $NaNO_3$. Strip R was adjusted to pH 7, because the addition of copper to 0.05M DTPA liberated enough acid to precipitate the complexing agents if the pH were much lower. DTPA neutralized to pH 7 contains nearly 3 Na^+ per molecule; the concentration of Na^+ in

Strip R is therefore about 0.15M. The ratio M_R/M_L (in this case also Na_R/Na_L) is thus ~0.5, as is the distribution coefficient D_L^R of silver (Equation 10). The flow ratio of the R and L strip streams was adjusted so that the extraction factor E_L^R for silver was ~0.12, and the flow ratio between the feed and the Strip R was adjusted to maintain 20% excess of complexing agent over copper.

The results in the following table demonstrate separations with four times the capacity obtained when the feed was introduced in the noncomplexing Strip L. The silver in the copper stream was small (but higher than in the preceding tests) and increased both when the feed rate was increased, and when the flow of Strip L was decreased while other flows were constant. This behavior is expected when silver is the ion transported across the membrane.

The concentration of copper in the silver stream (L) was generally lower than in previous tests, but much higher than expected; the Cu·DTPA complex is so stable no copper is expected to be transported into the silver product stream. The most reasonable explanation of the observed behavior is that the silver product was slightly contaminated with copper from previous tests in the same apparatus.

Two Complexing Agents (Method 4)

Although the preceding methods separated copper from silver quite well, still better results should be obtained if the sodium nitrate in Strip L were replaced by a specific complexing agent for silver. Unfortunately, complexing agents for silver normally complex copper even more strongly. This problem can be circumvented, however, by introducing the feed into the strip stream that contains an extremely powerful complexing agent for copper, such as DTPA. The copper reacts immediately to form the anionic complex $CuDTPA^{\equiv}$, which cannot be exchanged through the membranes. The silver ion, however, is uncomplexed and free to traverse the membrane. If another complexing agent for both silver and copper is used in the opposing strip solution, the silver will be concentrated preferentially in the opposing stream.

This concept was tested in a final experiment in which 0.1M $Na_2S_2O_4$ was used as the opposing strip stream; otherwise the process was identical to those discussed above.

This process gave the best over-all results obtained thus far. Both the silver and copper product streams contained very little of the other element. The silver product was more concentrated than in the previous tests because the presence of a complexing agent in Strip L increased the distribution coefficient of silver toward that stream and thus permitted a large reduction in flow.

No additional tests are planned on the separation of silver and copper, but information from this study will be used in future work on the separation of the actinide elements from some of the rare earths.

Separation of Silver and Copper by Complexing

Feed introduced into the DTPA stream
A Feed (R) 0.1M $Cu(NO_3)_2$, 0.1M $AgNO_3$
A Strip R 0.05M DTPA, pH 7

Flow, ml/min			Ag Product L β		Cu Product R A	
Feed	Strip L β	Strip R	Molarity Ag + Cu	Cu, mole %	Molarity Ag + Cu	Ag, mole %
Strip L 0.3M $NaNO_3$ (Method 3)						
0.1	1.0	0.22	0.0306	1.3	0.058	0.12
0.2	2.0	0.44	0.0159	1.4	0.037	0.06
0.4	4.0	0.88	0.00856	0.22	0.0309	1.1
0.4	3.0	0.88	0.0108	0.18	0.0310	1.8
Strip L 0.1M $Na_2S_2O_3$ (Method 4)						
0.4	1.0	0.88	0.038	0.15	0.0305	0.09 ✓

ION EXCHANGE MEMBRANE SEPARATIONS

The importance of flow-pulsing was confirmed for increasing the effectiveness of ion exchange dialysis as a means of concentrating solutions of uranyl nitrate. The dialysis technique -- based on Donnan equilibrium across ion exchange membranes -- is readily adaptable to continuous operation, a distinct advantage over the present batchwise concentration with ion exchange columns. Previous tests were summarized most recently in the November report (p 70).

A new dialysis assembly was constructed to demonstrate the effects of pulsing and several other design and operating conditions.

Apparatus

In the new assembly, the flow of the stripping (and product) solution along one face of the ion exchange membrane is always countercurrent to that of the feed (and raffinate) solution along the opposite face, rather than alternately cocurrent and countercurrent as in the earlier apparatus. The thickness and width of the flow channels can be varied easily; bypassing of regions of the membrane and leakage between the streams have been eliminated. The assembly is designed for study of process variables under nearly ideal conditions to provide data for design of a prototype plant-scale separator.

As shown in Figure 37, each of the five sections of ion exchange membrane, 37 inches long by 2 inches wide, is positioned by two polyethylene spacers that form the flow compartments between 1/2-inch-thick plates of stainless steel. Each plate has an inlet and an outlet drilled through the appropriate face and side, near each end, to provide for the countercurrent flows of the two solutions.

The polyethylene spacers can have any thickness and the contained 36-inch-long flow channel can have any width up to ~1.5 inches. In the present apparatus the spacers are 1/16 inch thick and the channels are 1/2 inch wide. The membranes are "AMFion"* C103C. The total length of exposed membrane is 15 ft and the area is 90 in^2.

Effect of Pulsing

The flow of the feed stream was pulsed in tests with feed containing 0.01M $UO_2(NO_3)_2$ and a stripping stream containing 2M HNO_3. The pulsing provides direct agitation of the flowing

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* Trademark of American Machine and Foundry Co.

[redacted]

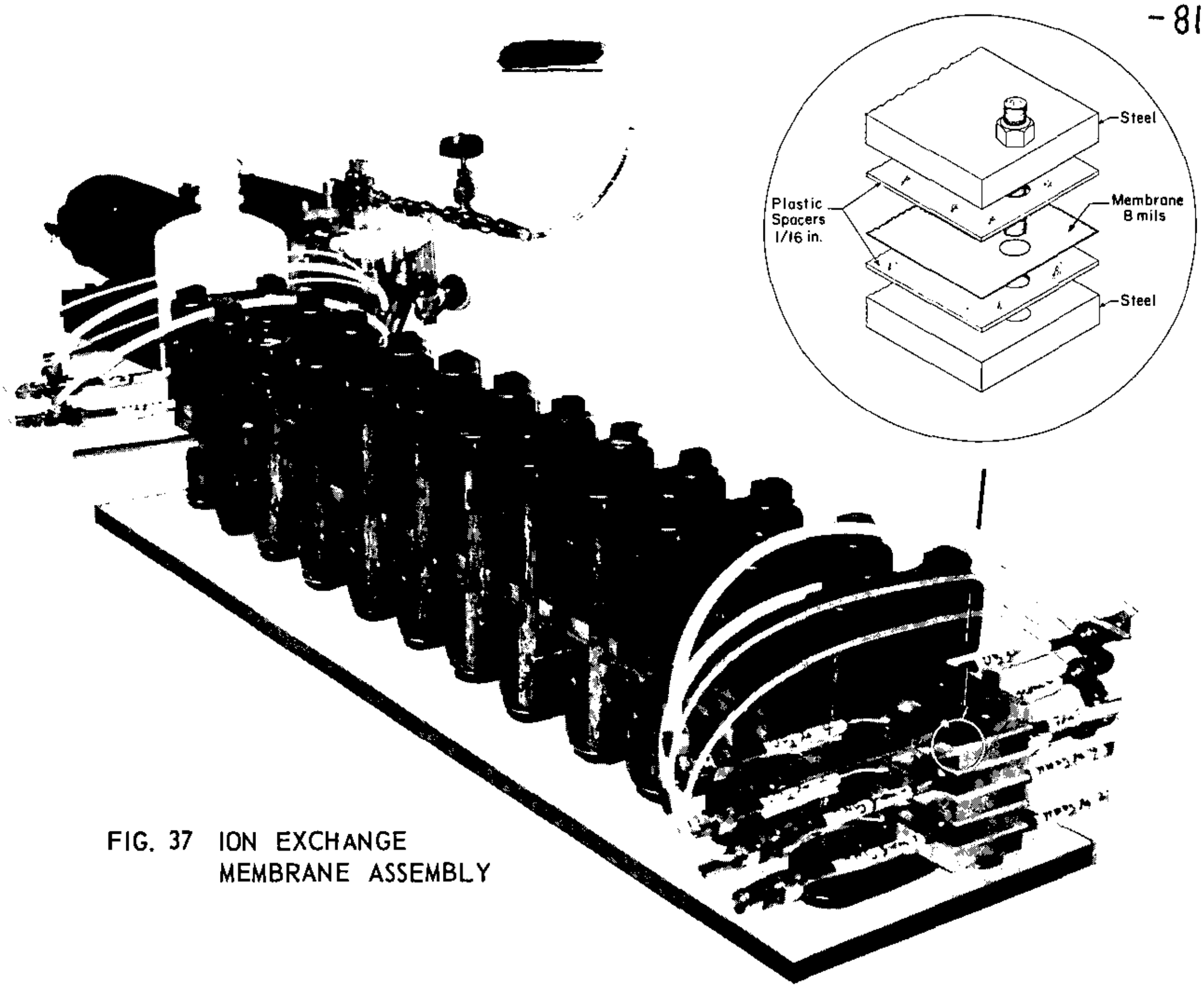

FIG. 37 ION EXCHANGE MEMBRANE ASSEMBLY

feed solution, and indirect agitation of the flowing stripping solution by flexing the membrane.

Steady-state concentrations in the effluent raffinate and product were obtained in ~24 hours. At steady state, the results with the present apparatus were very similar to those obtained with the previous device (June 1965 report, p 52 and October report, p 82), when normalized to equal area of membrane.

In a series of tests to determine the effect of the degree of pulsing on the concentration of uranyl ion, the feed flow was maintained at 6 ml/min and the stripping flow at 0.090 ml/min. The combination of concentrations and flows gave a value of

$$\alpha = C_o g_o \big/ 2U_F g_F = 1.5$$

where U_F = concentration of uranium in feed
g_F = flow of feed
C_o = concentration of nitric acid in stripping solution
g_o = flow of stripping solution

- [redacted] -

[redacted]

[redacted]

The parameter α determines the efficiency of operation and is optimum at ~1.5, as explained in the June 1965 report (p 52). Each test was continued for 24 hours to ensure steady-state conditions.

The results summarized in the following table show that pulsing increases the efficiency of the equipment for concentrating uranium. The primary effect of increased pulsing is to reduce the residual uranium in the raffinate; this is reflected also as a higher concentration in the product.

The efficiency is a direct function of the gross pulse flow, and is not affected significantly by the rate of pulsing at constant pulse flow. As shown in the table, virtually the same uranium was left in the raffinate at 30 and 90 pulses per minute when the amplitude was adjusted to maintain the same gross pulse flow.

Effect of Pulsing on Ion Exchange Dialysis

Feed 0.01M $UO_2(NO_3)_2$; 6.0 ml/min

Strip 2.0M HNO_3; 0.090 ml/min

Pulsing Conditions			UO_2^{2+} in End Streams	
Frequency, min^{-1}	Amplitude, ml	Flow, ml/min	Product, M	Raffinate, % of feed
0	0	0	0.180	23.0
30	1.0	60	0.275	7.0
30	2.25	135	0.281	3.6
30	4.5	270	0.280	1.9
90	1.5	270	0.313	1.5
90	3.0	540	0.315	1.2

The uranium in the raffinate decreased rapidly as the gross pulse flow was increased from low values but approached a constant value at high flow; gross flow higher than ~300 ml/min in the present apparatus has little benefit. This effect indicates that at low pulse flow the transfer of uranium is limited by slow diffusion through the solution to the membrane, but at high pulse flow the transfer is limited by diffusion through the membrane.

The rate of attainment of steady state is being studied in more detail, and the effect of variations in thickness of the stripping solution channel on the rate of this attainment is being determined.

- [redacted] -

[redacted]

ION EXCHANGE MEMBRANE SEPARATIONS

This section summarizes the progress since September to develop Donnan dialysis equipment for ionic concentration and separation processes in the plant. A complete process was demonstrated earlier in the laboratory for concentrating uranyl ions in the solvent extraction products to solutions of ^{235}U or ^{233}U suitable for conversion to uranium oxide or metal (October 1965 report, p 82); and several dialysis processes were demonstrated for separating Cu^{2+} and Ag^{+} ions (November 1965 report, p 70). The latter techniques appear to be applicable for separating such nuclides as curium from americium or possibly such groups as lanthanides from actinides.

Membrane dialysis has the principal potential advantages of continuous ion exchange operation and ease of replacement of the ion exchanger. Adaption to plant use depends upon development of small compact equipment that will operate reliably, and in which the membranes can be easily and remotely replaced. Two programs are underway to develop such equipment: one with flat commercial membranes (page 54), the other with tubular membranes not yet available commercially (page 61).

Flat-Membrane Separators

Flat-membrane apparatus for study of various design and operating conditions in continuous concentration of uranyl nitrate by dialysis was described in the September 1966 report (p 86). The importance of pulsing flow for increasing the effectiveness of the process was demonstrated. Further experiments with this apparatus have shown that:

> The rate of attainment of steady state is increased by decreasing the thickness of the flow channel for the stripping solution.
>
> In the absence of pulsing, loss of uranium to the raffinate is controlled by slow diffusion within the feed channels (if the channels are thick).
>
> Pulsing flow is unnecessary if the feed channels are sufficiently thin (~15 mils).