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METHOD FOR RECOVERY OF
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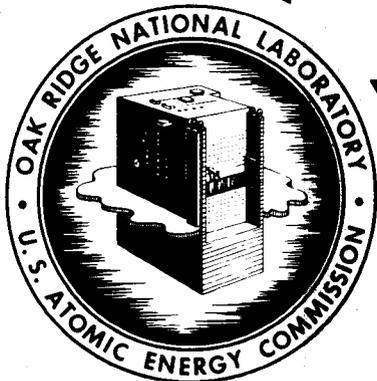
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Contract No. W-7405-eng-26
CHEMICAL DEVELOPMENT SECTION
CHEMICAL TECHNOLOGY DIVISION

A COMBINED DISTILLATION-ELECTROCHEMICAL METHOD FOR
RECOVERY OF HYDROFLUORIC ACID

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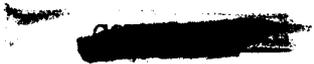
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1.0 ABSTRACT

Electrodialysis in an ion-exchange membrane cell was shown to be technically feasible for the concentration of an azeotropic mixture of HF and water. A flowsheet is presented for recovery of anhydrous HF by distillation and electro-dialysis of the azeotropic residue. In the electro-dialysis step, 2.6 kwhr of energy per pound of anhydrous product was consumed. With electricity at 1¢ per kilowatt-hour, the total operating cost of the electro-dialysis equipment alone, including amortization, would be 6¢ per pound of HF.

2.0 INTRODUCTION

The purpose of this investigation was to determine the feasibility of an electro-dialysis method for recovering anhydrous HF from the azeotropic HF-H₂O still residue resulting from the recovery of anhydrous HF by distillation. Water produced in the currently used process for hydrofluorination of UO₂ to UF₄ is separated from the excess HF in the effluent by partial condensation of 65-70% HF. This is either sold to the HF vendor on a contract basis or is distilled to return anhydrous HF to the process stream while the HF-H₂O azeotrope still residue, 38% HF (20.8 M), is neutralized with lime and discarded. The increasing amounts of 65-70% HF being produced in the expanding operations of the Atomic Energy Commission can be expected to greatly exceed the market for this material in the future. Distillation of greater amounts, with more efficient recovery, will therefore be desirable.

A simplified chemical flowsheet for the recovery of HF by distillation and electro-dialysis is presented. Optimum operating conditions for the electro-dialytic step of the process were investigated by studying the variation of HF transfer with temperature, current density, and steady-state concentration of HF in the diluting stream. Preliminary cost estimates were based on these data.

The analytical work on the program was done under the supervision of J. R. Wilson of the Analytical Chemistry Division, ORNL.

3.0 EXPERIMENTAL WORK

Electrodialysis may be defined as the mass transfer of ionic constituents of a solution across a diaphragm under an applied electric field. Permselective membranes, which are made of ion-exchange resin in sheet form, are excellent diaphragms for electrodialysis cells because of their high electrical conductivity, their resistance to hydraulic transfer of water, and their impermeability to the passage of un-ionized substances and colloidal material. Under an applied d-c potential, cation-exchange membranes allow passage of cations preferentially to anions; the reverse is true of anion-exchange membranes. When these membranes are stacked in an alternating pattern with electrolyte solutions separating them and a direct current is passed through the system, the solution is diluted in alternate cells and concentrated in the others, water being transferred by endosmosis in the direction of the ionic flow. More water is transferred than the water of hydration of the ions moved, but the induced flow is low enough to permit the membrane to operate as an efficient water barrier. The net effect is the stripping of water on passage through the membrane and a more concentrated electrolyte in the product. A large number of cells can be arranged between two electrodes to reduce the electrode voltage and surface to a minimum.

The electrodialysis unit used in these experiments consisted of six AR-111 anion- and seven CR-61 cation-exchange membranes, stacked one on top of the other in an alternating pattern. The anion membranes were cast on a dynel backing, and the cation membranes were backed with a saran grid. The anode was 0.0003-in.-thick platinum foil and the cathode was made from 1/16-in.-thick monel. The unit was arranged so that one manifold supplied a solution stream for concentration while a second manifold supplied the other solution stream for dilution. These streams were distributed into alternating cells through channels that were defined by the plastic gaskets separating the membranes. After the two solutions had passed across the membrane surfaces, they recombined in a second manifold system. Solutions

were supplied separately to the anode and cathode compartments (Fig. 3.1).

The solution streams were recirculated with Sigma pumps. Twelve-foot lengths of 1/4-in.-dia. monel tubing, coiled and inserted in a water bath, were connected to each line for temperature control. Pressure gages and thermometers encased in thin-walled tygon tubing were installed. Air traps were placed in each line just before the entry of the recirculating streams into the unit to absorb the pulsation caused by the steel fingers of the pump kneading the rubber tubes.

During a run, an Ionics constant-displacement pump controlled the rate of addition of solution to the diluting cells and to the electrode compartments. Solution was not fed to the concentrating cells, and effluent from these cells was due solely to solvent transferred during electro dialysis. Weir type overflow devices made from fluorothene emptied the influent solutions after they were completely mixed with the recirculating streams held up in the system piping. In the case of the electrode solutions these overflow systems also functioned as gas separators. Water-cooled condensers constructed of monel were inserted in the top of each overflow device to minimize loss of solution by evaporation.

Solution prepared by diluting 60% (36 M) HF, technical grade, to 38% was fed and current was passed until steady state was closely approached. Influent and effluent rates of solution flow were measured by the gain and loss in weight of the various samples during a fixed time interval. Representative samples for hydrogen determination were collected during steady-state operation.

The voltage of the cells between the electrodes was measured across two platinum tabs inserted before each of the electrode compartments. In the six-cell-pair laboratory model the voltage drop across the electrodes was a large fraction of the total voltage observed, but was neglected to permit a more accurate estimate of the energy and power requirements of the electro dialysis process. Commercial installations would use 100-150 cell pairs between electrodes, and the electrode voltage would be negligible compared with the total voltage of the unit.

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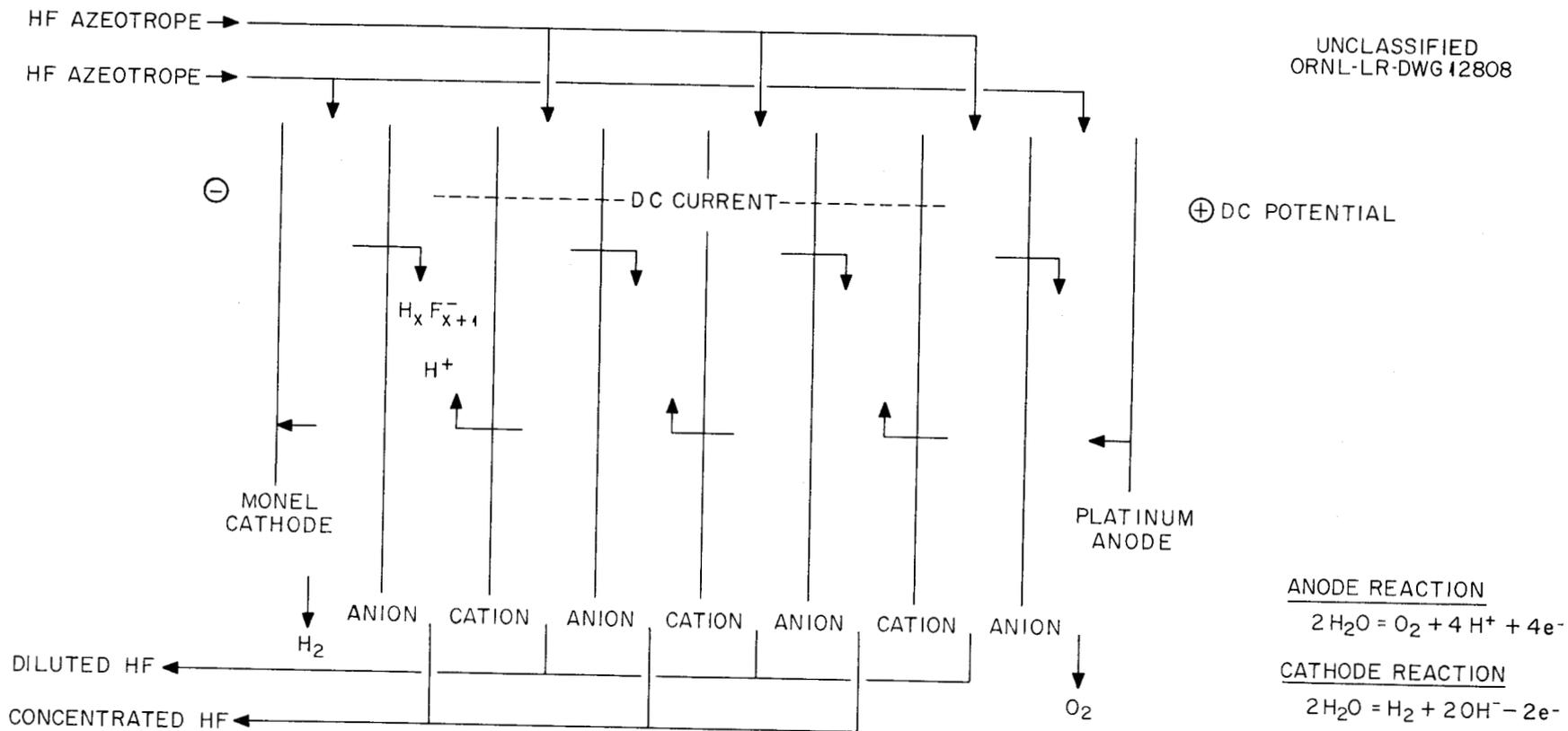


Fig. 3.1. Schematic Diagram of HF Concentration Electrodesis Unit.

The pressure drop across the unit in the separate solution streams was equalized at 5-6 psig by controlling the rate of recirculation. The temperature was controlled by varying the flow of cooling water into and out of the water bath. The steady-state concentration of HF in the cells in which dilution was taking place was controlled by varying the flow rate of the feed solution at a fixed current value.

Temperature (20-28°C) and HF concentration (18.88-19.75 M) were kept approximately constant to study the effect of current density on HF transfer. Current density (150 amp/ft²) and HF concentration (19.13-19.44 M) were kept constant to study the effect of temperature. The effect of fractional removal of HF from the stream being diluted was studied at constant current density (150-180 amp/ft²) and temperature (25-27°C) by varying the influent flow rate by a factor of 2.

4.0 RESULTS

Experimental conditions are summarized in Table 4.1 which is divided into three parts to emphasize the operating variable under investigation. The results are given in Table 4.2 and plotted in Figs. 4.1 - 4.3.

As the current density increased, the current efficiency, rate of solvent transfer, and concentration of HF transferred also increased (see Table 4.2 and Fig. 4.1). The current efficiency increased more rapidly than the rate of solvent transfer per unit of current, which caused the increase in the molarity of the HF transferred. Increasing the temperature decreased the concentration of HF transferred (Table 4.2 and Fig. 4.2) as a result of a less rapid increase in current efficiency (35%) than in solvent transfer (45%). Increasing the concentration differential of the HF influent and effluent in the cell where dilution was occurring decreased the concentration of HF transferred. The current efficiency did not change while the solvent transfer rate increased (Table 4.2 and Fig. 4.3) at two similar current density values (150 and 180 amp/ft²) but at two different flow rates with

Table 4.1 Experimental Conditions Used in Study of Electrodialytic Transfer of HF

Exp.	Current (amp)	Voltage (volts)	Flow Rate (ml/min) in Electrode Compartments		Current Density ₂ (amp/ft ²)	Temp (°C)	Flow Rate (ml/min)				HF Concentration (M)			
							Diluting cell		Concentra- ting cell		Diluting cell		Concentra- ting cell	
			In	Out			In	Out	In	Out	In	Out		
Variation in Current Density														
11	17	2.2	12.30	9.87	75	20	13.17	9.53	0	3.47	20.63	19.75	Same as diluting cell in	23.09
12	34	5.0	12.20	13.28	150	28	26.44	17.87	0	7.09	20.54	19.14		24.14
13	40	4.8	14.00	13.15	180	27	30.28	21.57	0	8.78	20.40	18.88		24.12
20	45	5.7	15.85	15.00	200	26	34.20	24.00	0	10.26	20.79	19.04		24.38
Variation in Temperature														
19	34	5.2	12.54	12.50	150	12	27.08	20.30	0	6.60	20.82	19.44	Same as diluting cell in	24.08
17	34	4.2	12.24	12.10	150	40	27.00	18.33	0	8.17	20.50	19.13		23.69
18	34	3.7	12.31	11.60	150	55	26.81	16.97	0	9.41	20.67	19.19		23.40
Variation in Feed Rate of HF to Diluting Cell														
15	40	5.4	12.55	12.28	180	27	12.97	3.22	0	9.44	20.55	15.99	Same as diluting cell in	22.42
14	34	4.5	12.37	12.33	150	25	13.00	4.97	0	7.42	20.32	17.22		22.92
16	34	4.4	12.50	12.10	150	26	26.82	19.52	0	7.13	20.93	19.52		24.36

Table 4.2 Results of Electrodialytic Transfer Study

Exp.	Variable	Rate of Transfer		Current Efficiency (%)		Rate of Volume Transfer (ml/min)		Molarity of HF transf'd (meq _{Ch} /Vol. Tr)		
		Elec (meq _{El} /min)	Chem. (meq _{Ch} /min)		(meq _{El} × 100/meq _{Ch})		(ml/min)		(meq _{Ch} /Vol. Tr)	
			Diluting cell	Concentrating cell	Diluting cell	Concentrating cell	Diluting cell	Concentrating cell	Diluting cell	Concentrating cell
Effect of Variation in Current Density										
11	75 amp/ft ²	63	84	80	132	126	3.64	3.47	23.05	23.09
12	150 amp/ft ²	127	201	171	158	135	8.57	7.09	23.45	24.14
13	180 amp/ft ²	149	211	212	141	141	8.71	8.78	24.25	24.12
20	200 amp/ft ²	168	254	250	151	149	10.20	10.26	24.90	24.38
Effect of Variation in Temperature										
19	12°C	127	170	159	134	125	6.78	6.60	25.05	24.08
17	40°C	127	204	194	160	153	8.67	8.17	23.55	23.69
18	55°C	127	230	220	181	173	9.84	9.41	23.40	23.40
Effect of Variation in Feed Rate of HF to Diluting Cell										
15	12.97	149	215	212	143	141	9.75	9.44	22.00	22.42
14	13.0	127	179	170	141	134	8.03	7.42	22.30	22.96
16	26.82	127	181	174	142	137	7.30	7.13	24.80	24.36

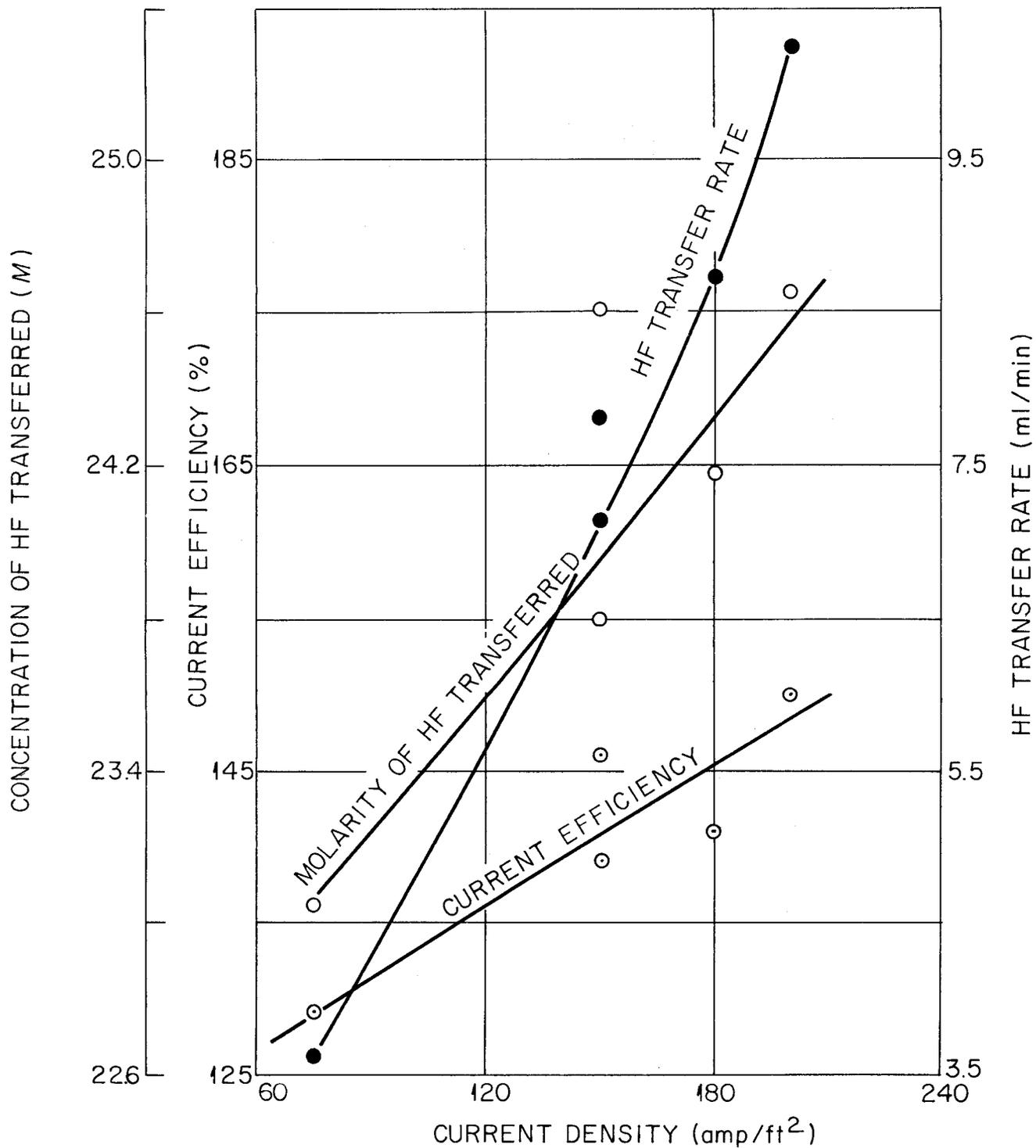


Fig. 4.1. Variation of HF Transfer Parameters with Current Density.

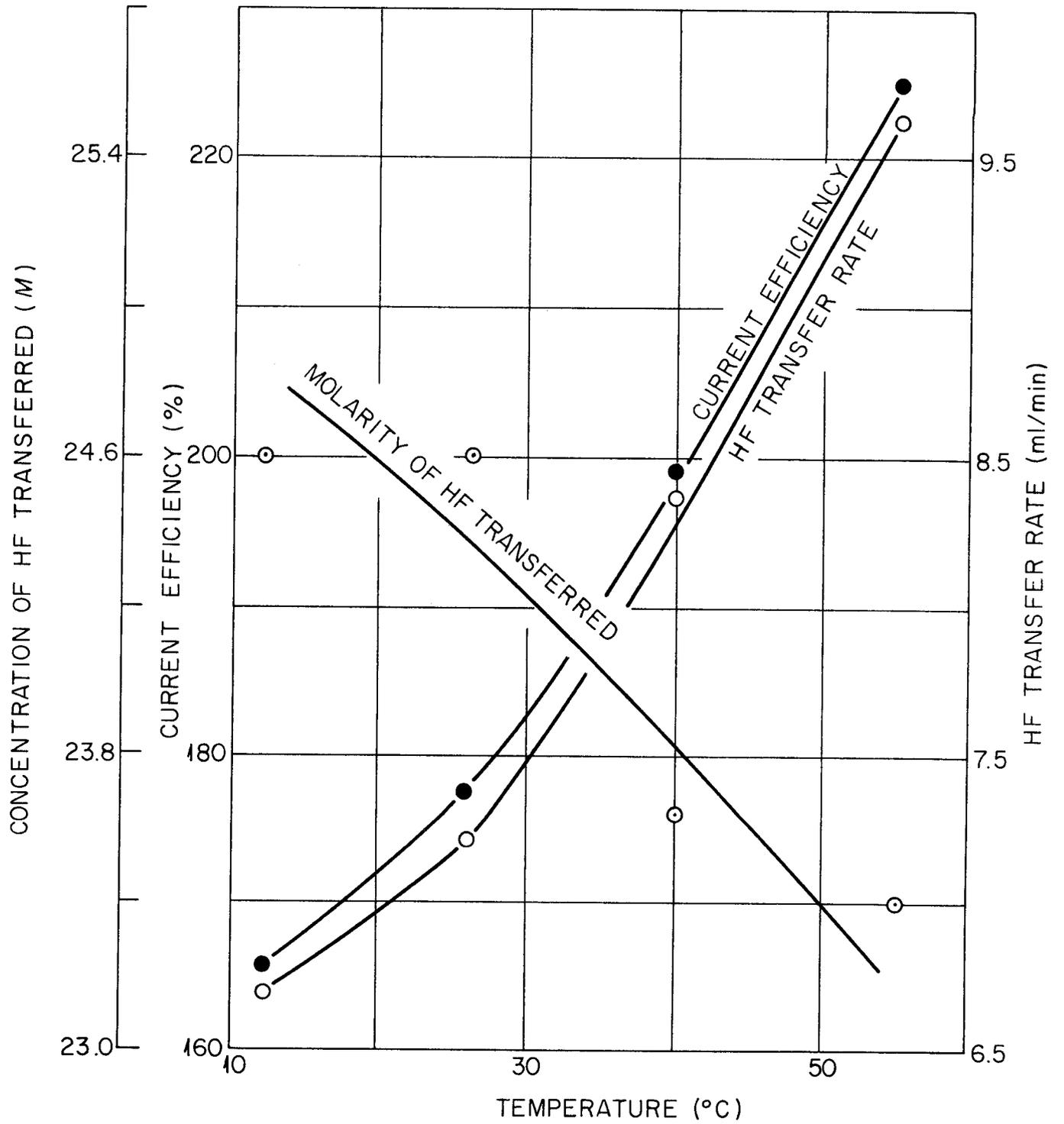


Fig. 4.2 Variation of HF Transfer Parameters with Temperature.

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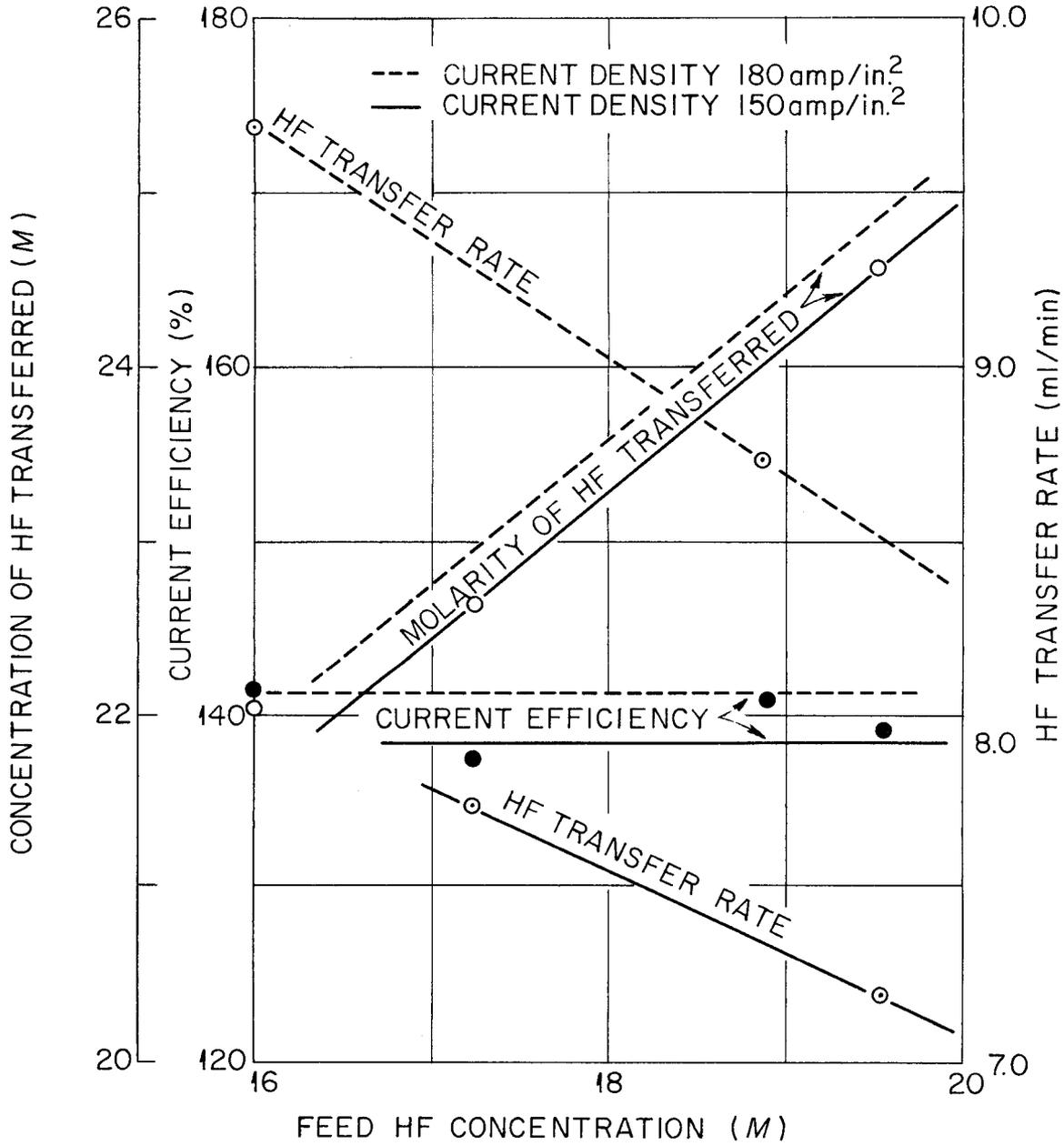


Fig. 4.3. Variation of HF Transfer Parameters with Feed HF Concentration.

the higher fractional removal of HF from the stream being diluted, the effluent concentration of the stream being concentrated was lowered.

5.0 CHEMICAL FLOWSHEET FOR DISTILLATION- ELECTRODIALYSIS RECOVERY OF HF

The scheme projected for a distillation-electrochemical process for the recovery of anhydrous HF is shown in Fig. 5.1. The HF condensate from the uranium dioxide hydrofluorination reaction (955 lb/hr) is sent to a still. The anhydrous HF (455 lb/hr) that is evolved is returned to the process stream, and the azeotrope that is also produced in this still (500 lb/hr) is condensed and transferred to a membrane demineralizer. The azeotropic mixture is concentrated in the membrane unit, and the concentrated effluent stream is returned to the still to evolve 190 lb/hr more of anhydrous HF. The diluted stream is sent to a second still where it is concentrated to the azeotropic mixture and returned to the demineralizer for further concentration and for removal of 310 lb of H₂O per hour.

6.0 PRELIMINARY COST PROJECTION FOR ELECTRODIALYTIC HF RECOVERY

Economic operation of the distillation-electrodialysis scheme for the recovery of anhydrous HF depends on the efficiency of concentration of the HF azeotrope in the ion-exchange-membrane demineralizer since the sizes of the still and the membrane unit required are directly dependent on the performance of the unit. For example, a large separation of HF and H₂O in the demineralizer reduces the inventory or recycle of azeotrope, thereby reducing the size requirements of the unit and vapor stills. Investment and operating costs are decreased as a result.

The optimum result of the experimental program (run 20) was used as a basis for a preliminary cost estimate of the electro dialysis step for HF

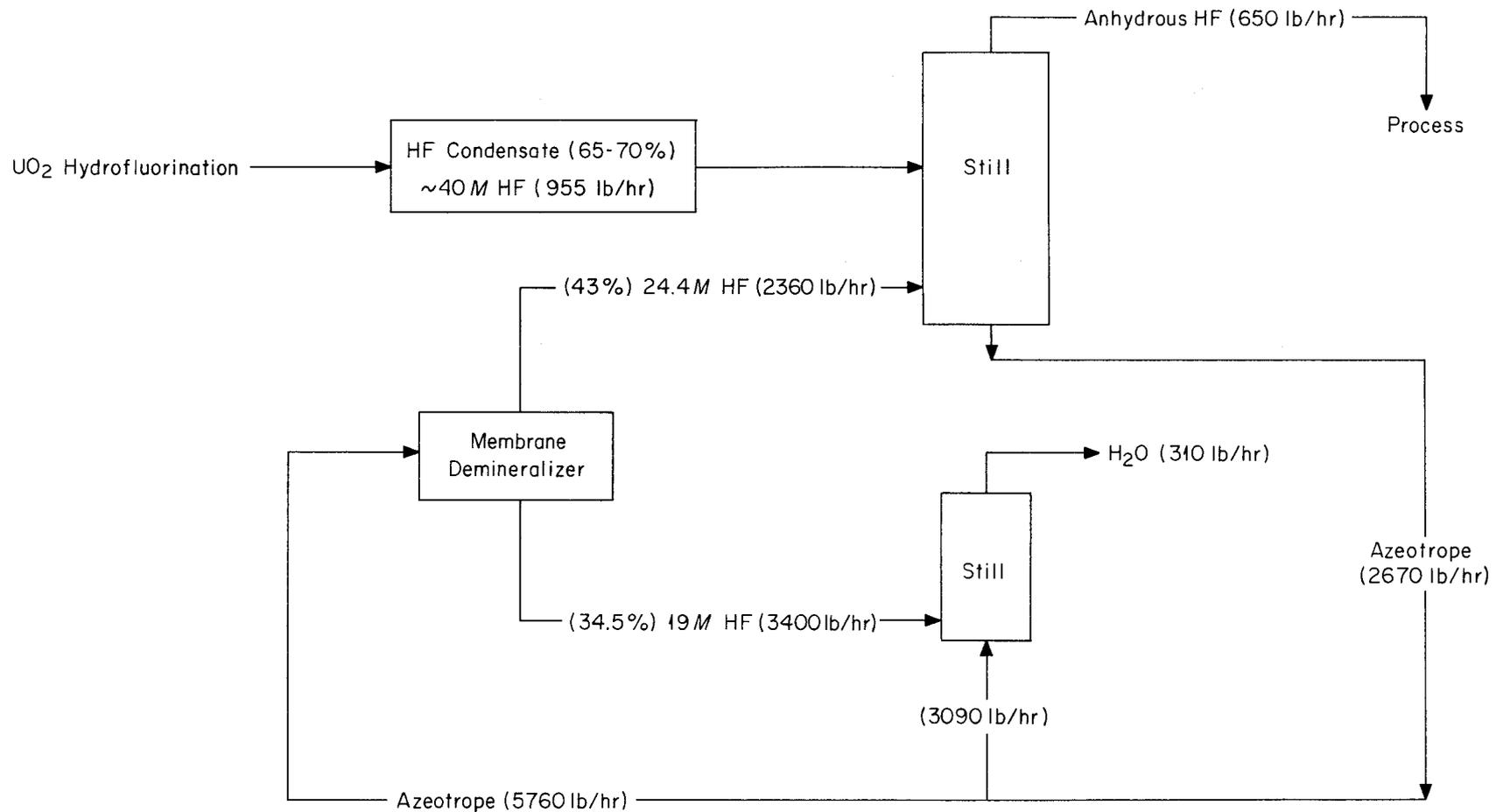


Fig. 5.1 Chemical Flowsheet for Electrochemical-Vapor Distillation Method for Recovering Anhydrous HF.

recovery (Table 6.1). The additional recovery of 190 lb of anhydrous HF per hour from 500 lb of azeotrope produced during recovery of 455 lb of anhydrous HF by the distillation of 955 lb of 65-70% HF condensate per hour from the UO_2 hydrofluorination reaction was the rate of operation considered. The rate of power and membrane area utilization in the laboratory experiments was a basis for the calculations. The membrane and gaskets were amortized at 100% per annum. All other standard equipment was amortized at 16% per annum.

7.0 PROCESS EVALUATION

The distillation-electrodialysis process that has been proposed as a method for recovery of HF is technically feasible. However, the projected chemical flowsheet and the cost projections for HF recovery based on data obtained during this study indicate that this process, as it stands, is not sufficiently economical. To recover an additional 190 lb of anhydrous HF per hour, the original still, which handles 955 lb of 65-70% HF and already recovers 455 lb of anhydrous HF per hour, must be expanded to accommodate an additional 2360 lb of material per hour; a second still to handle 3400 lb of dilute HF per hour must be incorporated in the system; and electro-dialysis equipment involving 2560 ft² of current effective membrane area is required. For economic recovery, a considerably greater concentration of HF than was obtained in the membrane demineralizer would be necessary.

Table 6.1 Preliminary Cost Projection for Electrodialysis
Step of HF Recovery Process

Basis: recovery of 190 lb of anhydrous HF per hour from
20.8 M azeotrope

Initial Investment

Electrodialysis equipment ^a at \$40 per ft ² <u>b</u>	\$102,400
Rectifier at \$100 per kw	50,000

Operating Cost (\$ per lb of anhydrous HF)

Amortization of electrodialysis equipment at 16% per year	\$ 0.012
Amortization of rectifier at 16% per year	0.006
Membrane and gasket replacement (\$10 per ft ²) at 100% per year	0.019
Energy at 1¢ per kwhr	<u>0.026</u>
Cost per pound of anhydrous HF	\$ 0.063

^a-Electrodialysis equipment includes pumps, tanks, and piping as well as all cell components (exclusive of membranes and gaskets).

^b-Current effective area.