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HYDROGEN ISOTOPE SEPARATION BY BIPOLAR ELECTROLYSIS WITH COUNTERCURRENT ELECTROLYTE FLOW*

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ABSTRACT

Separation of hydrogen isotopes has been successfully demonstrated using bipolar electrolysis combined with electrolyte flow countercurrent to the transport of hydrogen isotope species. Use of multibipolar electrode cells in a squared-off cascade is shown theoretically to be capable to efficient tritium separation. Experimental operation of multibipolar cells and analysis of their operation by McCabe-Thiele techniques is described.

INTRODUCTION

Bipolar electrolysis using an electrode that is permeable to hydrogen has been suggested (1-6) as a possible method for the separation of hydrogen isotopes. It is the character of the bipolar electrolytic process that multiple separation of hydrogen isotopes can be realized within a single electrolysis cell with the formation of gases only at the terminal anode and

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cathode. This technique offers a much simplified material flow between separation stages as compared to conventional electrolysis, where gaseous products evolve from every separation stage and subsequently must be converted to water before entering the adjacent stages. An additional major advantage of the bipolar process is the ability to consume less power than conventional electrolysis having equivalent separative capability.

If a conductive barrier is inserted between the terminal electrodes of a conventional electrolysis cell in such a way as to isolate one electrode from the other, the barrier is forced to act both as an anode and cathode, i.e., to become "bipolar." A bipolar electrode material such as Pd-25 wt. % Ag can readily sorb and diffuse hydrogen, so that molecular hydrogen will not form at the cathode interface. At the anode surface the diffused hydrogen atoms are oxidized to form water with the hydroxyl ion present in the electrolyte (see Fig. 1). The electrode processes and the permeation of hydrogen through the bipolar electrode favor lighter isotopes and therefore isotope separation results.

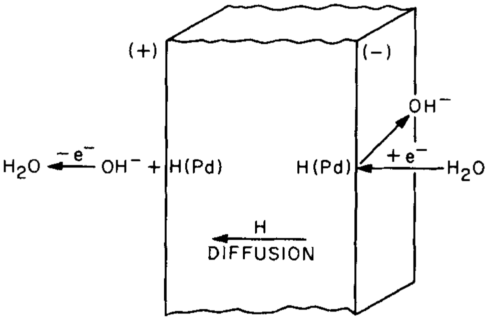

FIGURE 1. Hydrogen transfer mechanisms occur at and in the bipolar electrode.

SEPARATION FACTOR DETERMINATIONS

Hydrogen isotope separation with a Pd-25% Ag bipolar electrode represents a modified case of normal electrolytic hydrogen isotope separation. Because of the different mass transfer mechanisms involved, a different separation factor from that observed during normal electrolysis may result. The experimental measurements of deuterium-tritium separation factors (α_{DT}) obtained at three different temperatures and at current densities of 0.21, 0.36, and 0.50 A cm^{-2} are given in Table 1. These data represent the average values of twenty-five individual measurements. No significant dependence of α_{DT} on current density was found, and only small dependence on temperature was observed. Several measurements of the hydrogen-tritium separation factor, α_{HT} (see Table 1), were performed with little or no temperature dependence being noted.

The magnitude of the bipolar separation factor is approximately the same as for normal electrolysis. However, the normal electrolysis separation factor is more dependent on temperature than the bipolar electrolysis separation factor. It is suspected that this phenomenon is attributed to the different mass transfer mechanisms of bipolar electrolysis. These results are of importance in that the operation of a bipolar system at

TABLE 1

Hydrogen Isotope Separation Factors on a Single Bipolar Electrode

Temperature °C	α_{DT}	α_{HT}
30	-	11.7 ± 1.0
35	2.13 ± 0.05	-
55	2.09 ± 0.03	10.8 ± 0.7
90	2.02 ± 0.03	11.4 ± 0.5

high temperature and high current density to achieve high throughput can be done without significant loss of separative efficiency.

POWER CONSUMPTION CONSIDERATIONS

A major advantage of the bipolar process is its ability to consume less power than equivalent conventional electrolysis. This reduction in power consumption is possible because of different electrochemical reactions occurring at and within the bipolar electrodes as compared with those of normal electrolysis. In conventional water electrolysis, the net standard potential is -1.229 volts, whereas the net standard potential for bipolar electrolysis is zero; the only additional potential required is the "overpotential" necessary to drive the reaction at an appreciable rate. In addition, no gas is formed at either surface of the bipolar electrode and therefore the potential drop at the electrode-electrolyte interface is reduced.

Power consumed by an electrolytic cell is the product of the total cell voltage and the cell current. However, a direct comparison of power consumption of bipolar electrolysis with normal electrolysis based solely on their respective single cell voltages should not be made. For one reason, when using the bipolar electrode concept as a multistage separation system, it must be remembered that a bipolar electrode cannot exist without the usual terminal electrodes. Therefore the total voltage of a multistage bipolar system will always include the voltage associated with one normal electrolysis cell. In order to compare bipolar electrolysis power consumption, consideration must be given to the specific separation task and to how bipolar electrolysis can best approximate an ideal separation cascade. Such an analysis of power consumption will be shown in the following sections.

MULTIBIPOLAR CELL THEORY AND EXPERIMENTAL RESULTS

A single bipolar electrode placed between terminal electrodes creates a cell with two separation stages; separation occurs at the bipolar electrode as well as at the terminal cathode. Addition of n bipolar electrodes establishes a bipolar "cascade" with J = n + 1 separation stages. With this arrangement, a flow of hydrogen isotopes (W) is established through the system toward the terminal cathode (see Fig. 2). Enrichment of the heavier isotope occurs in the aqueous phase adjacent to the cathodic side of each bipolar electrode. To achieve continuous isotope separation, aqueous material enriched in the heavy isotope must be swept away from the cathode surface and circulated through each electrolyte compartment countercurrent to the hydrogen transport. In practice the feed stream (F) enters the terminal cathode compartment and a product (P), enriched in the heavy isotope, is withdrawn from the terminal anode compartment such that F = W + P. (The W stream exiting from the terminal cathode compartment is depleted in the heavier isotopes with respect to the feed and may be considered the "waste stream.")

Steady-state cascade theory can be used to calculate the number of stages needed for the desired separation, the local

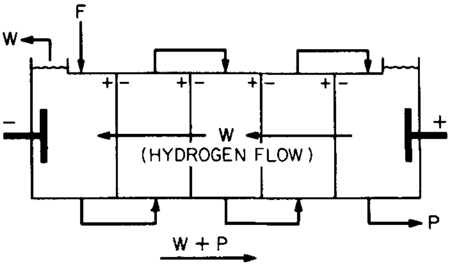

FIGURE 2. A schematic flow diagram of a bipolar electrolysis cascade for hydrogen isotope separation.

interstage flow rates, compositions, and other design details. A mathematical model was derived (5) specifically for bipolar electrolysis.

Total enrichment (i.e., total increase in heavy isotope concentration from feed to product) for the enriching section of a bipolar cascade with a flow scheme as illustrated in Fig. 2 may be expressed as

$$m_F = \beta m_P,$$

$$\beta = (1/\alpha\phi)^J + (1 - \phi) \left[\frac{1 - (1/\alpha\phi)^J}{1 - (1/\alpha\phi)}\right] \qquad (1)$$

where

m_F, m_P = mole fractions of the heavy isotope in the feed and product streams, respectively,

ϕ = $\dfrac{1}{1 - P/F}$,

α = single stage bipolar separation factor,

J = total number of separation stages in any section with stage number one being the bipolar electrode adjacent to the terminal anode.

Equation [1] is used to calculate the number of stages (J) necessary to enrich the heavy isotope to a desired concentration m_P and to calculate the interstage isotope composition in the electrolyte throughout a cascade.

Isotopes may exit the terminal-anode compartment either by the product stream (P) or by the stream of isotopes which permeate the bipolar electrode adjacent to the terminal anode. The product stream contains a known quantity of electrolyte. However, the isotope stream which exits through the bipolar electrode leaves the electrolyte behind. Therefore, the concentration of electrolyte in the product stream and in the terminal-anode compartment increases by a factor equal to the volume reduction ratio (F/P). With a typical F/P ratio of five or more, the electrolyte in the terminal-anode compartment will eventually solidify unless it is removed by an auxiliary process. Electrolyte buildup in any other interstage compartment will not occur because the electrolyte left behind by an exiting hydrogen isotope stream will be counteracted by a stream of hydrogen isotopes entering from an adjacent compartment.

Continuous electrolyte removal was demonstrated successfully in a long-term experiment using a spray drier-reactor as an integral part of the bipolar electrolysis cascade (5). In this auxiliary process, sodium hydroxide is continuously removed in a circulating loop system by conversion to sodium carbonate with CO_2. The water, as it is removed from the sodium carbonate by evaporation, is returned to the anode compartment.

Several laboratory experiments were performed using small multi-bipolar cells. In a typical experiment, the cell was initially filled with feed of equal tritium concentration to that which would be fed continuously to the cell during the experiment. After filling, the multi-bipolar cell was operated at constant current until steady state conditions were obtained. One such experiment with four bipolar electrodes (GF-7) was operated for a total of 24 days, 8 days of which were at steady state. Solving Equation [1] by trial and error, the single stage separation factor for experiment GF-7 was found to be $\alpha_{HT} = 6.3$. At the end of this experiment, samples taken from each interstage compartment were analyzed for tritium. Figure 3 shows the resultant tritium concentration profile through the cascade. In this case nearly all enrichment had taken place in the first two stages; the other three stages would have exhibited more separation performance if a smaller P/F ratio had been used. However, without continuously removing electrolyte from the anode compartment a relatively high P/F ratio was necessary.

Another multibipolar experiment (GF-9) was performed using a new cell design. This cell contained three separation stages

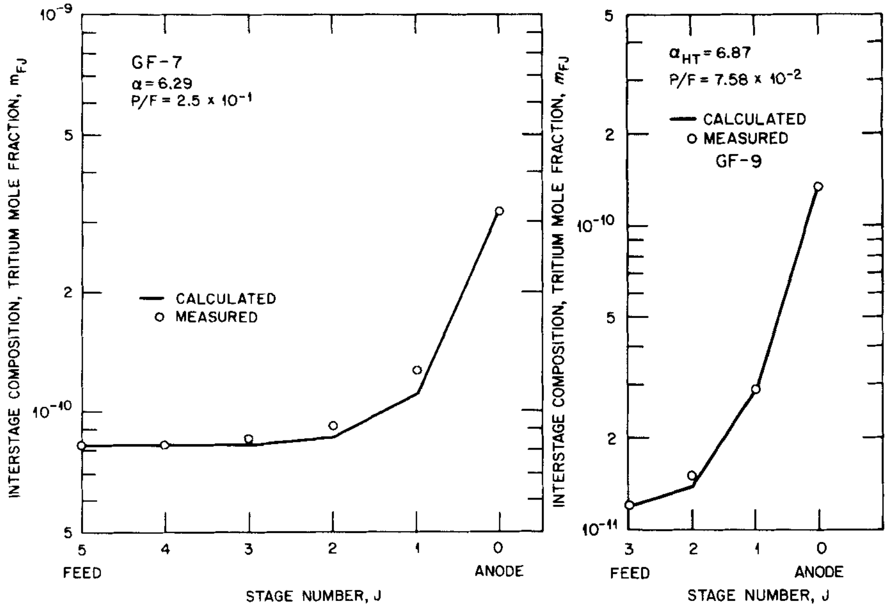

FIGURE 3. Interstage compositions occurring in bipolar cascade experiments GF-7 and GF-9.

(2 bipolar electrodes) and employed a continuous electrolyte removal system attached to the anode compartment. After 49 days of operation at a near total reflux condition (no product withdrawn), the system was forced to a steady state condition by withdrawing an increased amount of product. Experiment GF-9 was then operated for 8 days under these conditions to assure steady state composition throughout the cascade. Once again the experimentally observed tritium concentration between individual stages was closely predicted by Equation [1]. In this experiment more efficient separative utilization of all stages (as compared to experiment GF-7) was achieved, as shown in Fig. 3, as the result of using a lower P/F ratio (7.58 x 10^{-2}). The single stage separation factor was calculated from Equation [1] and found to be $\alpha_{HT} = 6.9$.

Single bipolar cell experiments indicated that at 90°C the protium-tritium separation factor, α_{HT}, should be 11 (see Table 1). In the multistage experiments described above, the single stage separation factors were calculated to be 6.3 and 6.9, respectively. No definitive reason for these lower separation factors can be given at this time; possible explanations could include backmixing in the cell. We have reason to believe that these low separation factors are not inherent with multistage bipolar electrolysis. Other multistage experiments with protium-deuterium have yielded a separation factor of approximately 5 which was what was expected at 90°C.

Comparison of the data from the two multistage cell experiments and the data as calculated by Equation [1] for these experiments, establishes Equation [1] as an accurate mathematical model for bipolar electrolytic isotope separation. An independent analysis of these same multistage cell experiments (8) has shown that modeling by using conventional McCabe-Thiele techniques is equally valid.

McCabe-Thiele analysis of experiment GF-7, Fig. 4, clearly illustrates that poor separation efficiency as observed for three of the five stages resulted from the operating line in the McCabe-Thiele graph being pinched to the equilibrium line at the feed point. The slope of the operating line is controlled by the P/F ratio [slope = 1/(1 - P/F)]. Figure 4 also illustrates the observed improvement in separation efficiency with the smaller P/F ratio used in experiment GF-9. Interstage compositions and the separation factors calculated using the McCabe-Thiele analysis agree very well with the data derived from Equation [1] and the tritium concentration profiles shown in Fig. 3. From these described analyses, it is evident that more efficient utilization of stages is achieved at a lower P/F ratio.

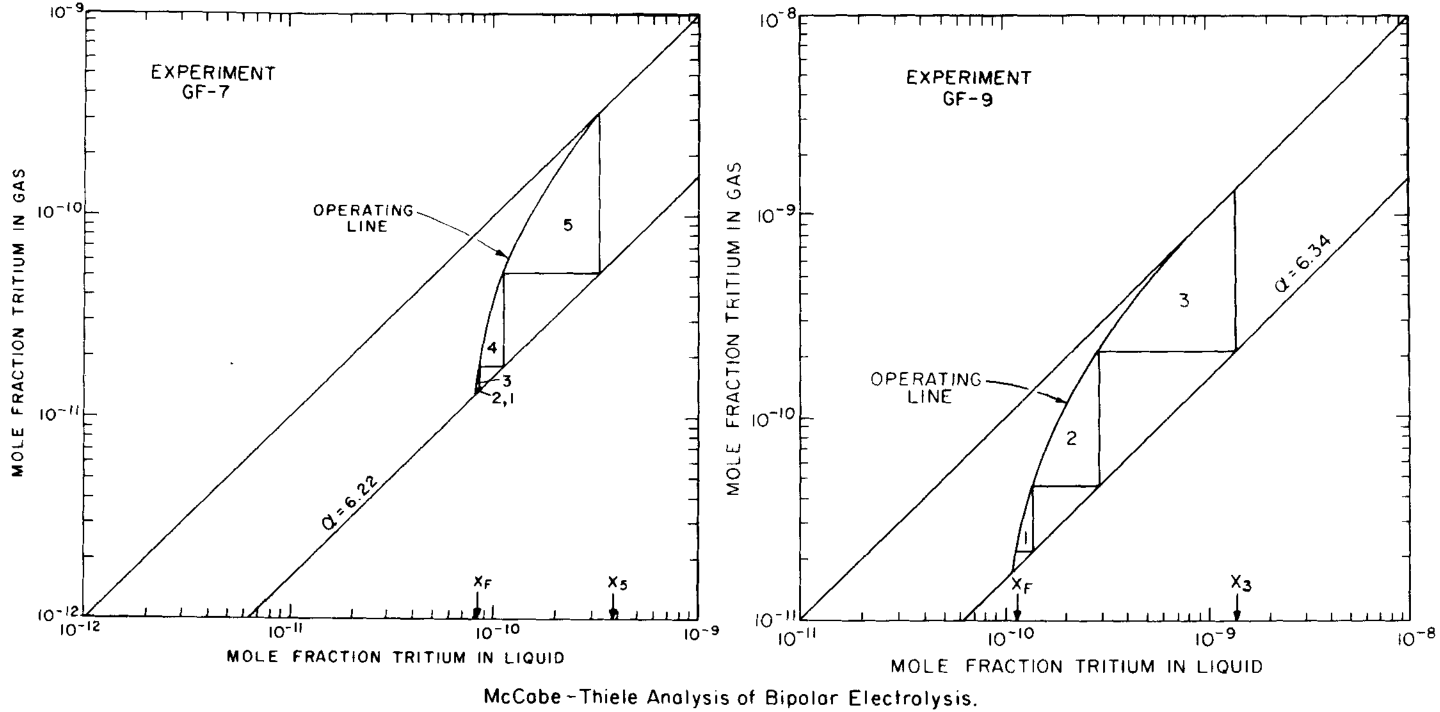

FIGURE 4. McCabe-Thiele analysis of multistage bipolar electrolytic separations.

OPTIMUM BIPOLAR ELECTROLYSIS CASCADE DESIGN

A multibipolar cell, as shown in Figure 2, is inherently a "square cascade", i.e., the mass flow (as defined by the constant current flow) is the same throughout the entire cell. Cascade theory (9) predicts that an ideal separation cascade should be tapered from stage to stage with a maximum cross section occurring at the feed point. This tapering is theoretically more efficient than a square cascade because total cascade volume and energy requirements are minimized. If a tapered cascade is not possible, its efficiency can be approximated by a "squared-off" cascade consisting of a series of square cascade sections of diminishing size from the feed point, connected in a series arrangement.

In a squared-off bipolar electrolysis cascade, there are $\underline{D}$ total square sections with $\underline{d}$ being any specific square section within the cascade (see Fig. 5). The square section with d = 1 is defined as the final enriching section of the cascade. Composition of the feed to section $\underline{d}$ of the cascade can be expressed as

$$m_{d+1,1} = (m_{d,1}\ B + C) \sum_{j=0}^{J_d - 1} A^j + m_{d,1}\ A^{J_d} \qquad (2)$$

where $A = (1 - \prod_{k=1}^{d} \rho_k)/\alpha$,

$B = \rho_d - (\rho_d - \prod_{k=1}^{d} \rho_k)/(1 - \prod_{k=1}^{d-1} \rho_k)$,

$C = \prod_{k=1}^{d-1} \rho_k\ m_p(\rho_d - \prod_{k=1}^{d} \rho_k)/(1 - \prod_{k=1}^{d-1} \rho_k)$,

$\rho_d = L_d/L_{d+1}$ the product to feed ratio for square section d,

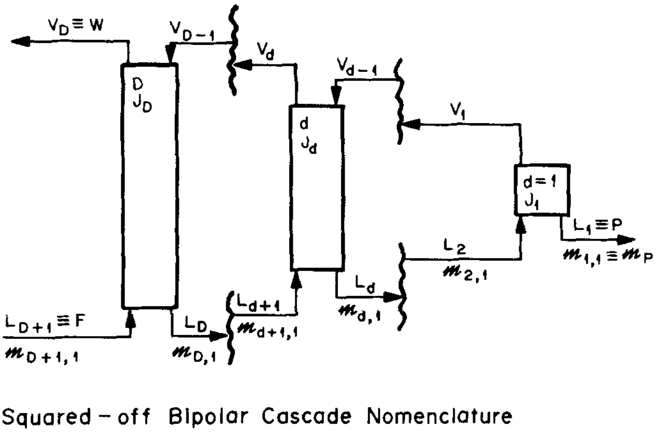

FIGURE 5. Squared-off bipolar cascade nomenclature.

$m_{d+1,1}$ = mole fraction of heavy isotope in stream used as feed for section d,

$m_{d,1}$ = mole fraction of heavy isotope in the product stream leaving section d,

J_d = total number of stages in section d,

$$\prod_{k=1}^{d} k = \rho_1 \rho_2 \cdots \rho_d \, .$$

Starting from the product end of the squared-off cascade, the feed composition to each square section can be calculated given J_d, ρ_d and α. Use of Equation [2] allows calculation of the concentration gradient through each square section.

In general, design of a squared-off cascade is accomplished by assuming that the optimum number of separation stages required for a specific enrichment can be described by ideal cascade theory. The total number of square sections and the number of separation stages per square section are then arbitrarily selected. The total number of separation stages in the squared-off cascade must equal the total number of stages of the ideal cascade. Using the mathematical model of a squared-off cascade (Equation [2]), adjustment of the product-to-feed ratio for each square section is performed such that the product stream composition of that square section matches the composition expected in the ideal cascade. Once this procedure is completed, the size of the separation cascade is fixed and the total power requirements for the assumed conditions can be calculated. The minimum power requirement for a particular enrichment is obtained by systematically repeating this procedure with varying numbers of square sections. The advantages of the bipolar separation process over normal electrolysis can best be illustrated by applying it to a specific separation task.

One possible specific application of bipolar electrolytic enrichment is the removal of tritium from heavy water used as the moderator and coolant in a nuclear reactor. The objective would be to reduce the tritium content in the coolant to an ultimate equilibrium tritium concentration of approximately one-sixth of its steady state level, e.g., reducing 20 Ci/l concentration to 3.3 Ci/l. Simultaneously, it would be desirable to enrich the tritium to 10 mole percent such that other established enriching methods could be used to eventually obtain pure tritium, which has intrinsic value.

The total electrolytic power required for a bipolar cascade system for this example is a function of the total number of square sections (D) as is shown in Figure 6. The minimum power requirement will occur in a range from $6 < D < 8$ for all values of the current densities shown. The minimum level of power required for this bipolar cascade would be less than that required for an equivalent ideal cascade with normal electrolytic cells*, e.g., at 0.3 A cm^{-2}, the power consumption for the

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*Data for the power required for normal electrolysis were taken from a review of commercial electrolysis by Lu and Srinivasan (10); data for power required for bipolar electrolysis are given in given in reference (5).

bipolar squared-off cascade could be expected to be approximately 75% of that consumed in normal electrolysis.

A design summary of the optimum squared-off bipolar cascade and an ideal cascade is given in Table 2. The optimum squared-off bipolar cascade was selected with D = 5 square sections, instead of 7, which would give the minimum power requirement. This was done because the size of the feed section is approximately 6% smaller and the total intersectional flows are approximately 14% less with 5 than with 7 square sections. Special consideration should be given to size differences of the cascades in that when tritium is being separated, containment of equipment to avoid personnel radiation exposure and ingestion is required, the cost of which diminishes with physical size. In particular, the cross-sectional area of the bipolar feed stage

TABLE 2

Comparison of Design Parameters for a Squared-off Bipolar Cascade and an Ideal Cascade[a]

	Ideal Cascade	Squared-Off Bipolar Cascade
Total Separation Stages	28	28
Number of Individual Sections	28	5
Cascade Feed Rate (1 D_2O/day)	2235	1541
Feed Point Cross Section (m^2)	92	64
Total Gas Flow; $D_2 + O_2$ (m^3/day)	14,100	3460
Total Electrode Material Cost (K$)[b]	61	151
Electrolytic Power (KW)	2006	1581
Electrolytic Power Cost ($/day)[c]	963	759
Total Intersection Aqueous Flow (1/day)	7627	1865
Electrolyte Maintenance Cost ($/day)	120	30
Electrolyte Recycle Rate, as Na_2CO_3 (kg/day)	2200	500

[a] Product flow rate 4.44×10^{-2} L D_2O/day; single stage separation factor $\alpha = 2$; current density 0.3 A cm^{-2}.

[b] Assumes 2.5×10^{-3} cm thick bipolar electrodes at 485 $/$m^2$ and 193 $/$m^2$ for normal electrolysis electrodes.

[c] Assumes 0.02 $/KWH power cost.

is 30% less than for an ideal cascade. The volume of gas generated using a squared-off bipolar cascade is only one-fourth of that incurred using an ideal cascade. Total flow of the enriched aqueous phase (intersectional aqueous flow) for the ideal cascade is approximately four times greater than that for the squared-off bipolar cascade; electrolyte maintenance cost and the electrolyte recycle rate reflect this same increase in magnitude. Thus the squared-off bipolar electrolysis cascade offers a smaller, more compact separation system which is expected to be easier and less expensive to maintain for radioactive containment.

The power cost for this bipolar cascade at 0.3 A cm^{-2} is estimated to be 21% less than for the ideal cascade, which is slightly higher than if 7 square sections were used (see Fig. 6). The relatively large savings in material flow appears to justify such an increase in power cost. This estimate is based on measured voltages across bipolar Pd-25% Ag electrodes (5). No special efforts were made to decrease the overvoltage at these electrodes. There are reasons to believe that this overvoltage may be lower if large real-surface area electrodes (such as porous Ni) were to be used. A reduction in overvoltage of 0.2 volts at 0.3 A cm^{-2} current density, for example, will yield a power consumption of 30% less than for the ideal cascade as compared to 20% less in our previous example.

SUMMARY

Palladium-25% silver alloy was found to be suitable as a material for bipolar electrodes permitting high hydrogen throughput with chemical and mechanical stability. Bipolar separation factors, at high current density, using NaOH (NaOD) as the electrolyte, are large (α_{DT} = 2.0, α_{HT} = 11 at 90°C).

Calculated mass transfer, as determined using a squared-off cascade model, together with observed electrical power con-

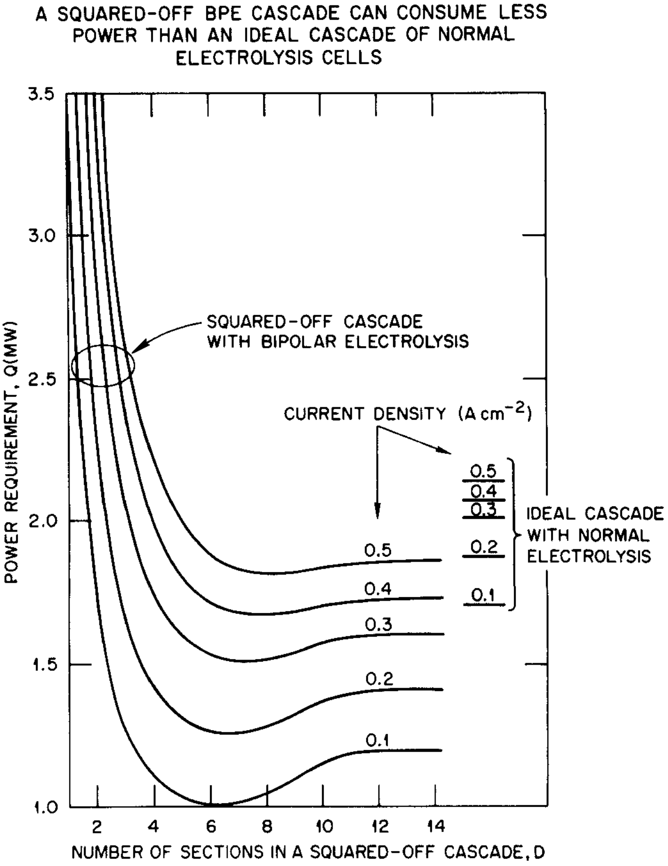

FIGURE 6. The minimum power required in our example for a bipolar electrolysis cascade for detritiation of heavy water will occur when the total number of square sections is between 6 and 8. In all cases the bipolar electrolysis power (curves) at their minimum are lower than the power required for a normal electrolysis cascade (short line segments at right).

sumption suggest that about 21 percent less power will be required for bipolar electrolytic separation as compared with normal electrolysis. This estimate only represents the present level of development.

Separation of tritium from light and heavy water using the bipolar electrolysis process appears to offer significant advantages as compared with direct electrolysis. The simplicity and efficiency of the multibipolar cell offer great potential for designing a very compact separation facility which, in turn, will miniize containment cost when high tritium concentrations are encountered.

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