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PRELIMINARY DESIGN AND ANALYSIS OF A
PROCESS FOR THE EXTRACTION OF LITHIUM FROM SEAWATER

by

Meyer Steinberg and Vi-Duong Dang

Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

September 1975

Presented at

"A Symposium on U.S. Lithium Resources and Requirements
by the year 2000"
U.S. Geological Survey, Denver, Colorado
January 22-24, 1976

MASTER

This work was performed under the auspices of the Controlled
Thermonuclear Division (CTR) of the U.S. Energy Research and
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Abstract

The U.S. demand for lithium by the industrial sector is estimated to increase from 2.7×10^6 Kg (3000 short tons) in 1968 to 1.2×10^7 Kg (13,200 tons) in the year 2000. Projections of the demand for lithium by a fusion power economy are subject to uncertainties in the future power demands of the U.S. and the wide range of requirements for various designs of controlled thermonuclear reactors (CTR). For a one million MW(e) CTR (D-T fuel cycle) economy, growing into the beginning of the next century (the years 2000 to 2030) the cumulative demand for lithium is estimated to range from $(0.55\text{--}4.7) \times 10^7$ to 1.0×10^9 Kg ($(0.6\text{--}5.1) \times 10^4$ to 10^6 tons). The present estimates of the available U.S. supply are 6.9×10^8 Kg (7.6×10^5 tons) of lithium from mineral resources and 4.0×10^9 Kg (4.4×10^6 tons) of lithium from concentrated natural brines. With this kind of demand approaching supply, there is concern for lithium availability in a growing CTR (D-T fuel cycle) economy. There is, however, a vast supply of lithium in seawater. Although the concentration

of lithium in seawater is dilute (170 ppb), the total quantity available is large, estimated to be 2.5×10^{14} Kg (2.8×10^{11} tons) thus insuring an unlimited resource for a long term fusion economy. These estimates provide the incentive for devising an economical process for the extraction of lithium from the sea.

A preliminary process design for the extraction of lithium from seawater is presented based on the literature data. The essential features of the process are that seawater is first evaporated by solar energy to increase the concentration of lithium and to decrease the concentration of other cations in the bittern which then passes into a Dowex-50 ion exchange bed for cation adsorption. Lithium ions are then eluted with dilute hydrochloric acid forming an aqueous lithium chloride which is subsequently concentrated. Lithium metal is then formed by electrolysis of lithium chloride. The energy requirement for lithium extraction varies between 0.08 and 2.46 kwh (e)/gm for a range of production rates varying between 10^4 and 10^8 Kg/yr. This energy requirement is relatively small when compared to the energy produced from the use of lithium in a CTR having a value of 3400 kwh (e)/gm Li. Production cost of the process is estimated to be in the range of 2.2 to 3.2 cents/gm Li.

To obtain a more definitive basis for the process design, it is recommended that a thorough phase equilibria study of the solid-liquid crystallization processes of seawater be conducted.

Uncertainties exist in the operation of large solar ponds for concentrating large quantities of seawater. A continued thorough search for a highly selective adsorbent or extractant for Li from low concentration aqueous solutions should be made. Investigation of other physical separation processes such as the use of membranes should be investigated.

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1. Introduction

The lithium industry was a small industry before World War II. During the war, it was necessary to develop a hydrogen storage means for the warships to lift equipment by balloon in case of emergency. Lithium hydride was developed for that purpose. A small amount of lithium hydride can react with sea water to release a large quantity of hydrogen (Hader, 1951). After the war, lithium requirement for nuclear purposes stimulated the production of lithium for some years during 1954-1960. Excess lithium produced in those years required more commercial end use after the need for lithium by the AEC decreased in 1960.

Commercial uses of lithium and its compounds are in the following categories (Cummings, 1968 and Shreve, 1967). Lithium itself is mainly used for ceramics, glass and multipurpose greases. Other commercial uses of lithium and its compounds are for automotive, metallurgy, air conditioning, batteries, etc.

Besides the commercial use of lithium, it is anticipated that lithium can be used as blanket material in the fusion reactor. Lithium has been proposed for the blanket material of the first wall of a fusion reactor (Controlled Thermonuclear Research Division, 1973) because its nuclear properties are ideal, its thermal conductivity is high, it is a desirable coolant, and above all, it is tritium breeding material. A major difficulty with lithium as a CTR coolant is its high electrical conductivity which leads to excessive pressure drop and pumping power in circulating it as coolant in the vicinity of the strong magnetic field of the plasma. To overcome this difficulty, Sze and Stewart (1974) proposed a method of electrical insulation. Other alternative methods (El-Wakil, 1971) are the use of lithium compounds which may be one of the following four materials: (1) molten salts such as LiF-BeF_2 eutectic called flibe, (2) lithium nitrates along with other nitrates, (3) mixtures of liquid metals and molten salts such as lithium and flibe, and (4) LiAl compound (Lazareth, et al. 1975).

Use of lithium for blanket or coolant material can be viewed from an energy point of view (Holdren, 1971). The basic deuterium-tritium reaction will release a neutron, an alpha particle, and an energy of 17.6 MeV carried by the neutron and alpha particle. Deuterium is available in seawater but natural

tritium is scarce. Bombardment by a neutron, lithium can be used as a breeder for tritium in the fusion reactor. Because of this characteristic, lithium becomes one of the unique elements in the fusion reactions. The energy value of one gram of lithium can be increased by increasing the breeding ratio (tritons produced/tritons consumed) or increasing the amount of energy per fusion. Lee (1969) estimated that the effective energy content of natural Li ranges from about 8.5×10^3 kwh(t) per gram to 2.7×10^4 kwh(t) per gram of natural lithium. Natural lithium consists of 7.5% Li^6 and 92.5% Li^7 .

2. Supply and Demand of lithium

Production of lithium for various commercial end uses has been described previously. Fusion power should be available at the turn of the century. Natural lithium demand for fusion reactors varies depending on the reactor type as is shown in Table 1. For a solid lithium blanket, the quantity required is about 5.5 ~ 46.8 Kg/MW(e) of natural lithium or 0.46 ~ 3.9 Kg/MW(e) 90% enriched in Li^6 depending on the first wall load and thermal conversion efficiency. For a liquid lithium blanket, the quantity required may be as high as about 1000 Kg/MW(e). It should be noted that the minimum activity solid blanket is 90% enriched in Li^6 while the liquid coolant blanket is natural lithium (7.5% Li^6). In the following, all the quantities of lithium expressed are in terms of the amount of natural lithium. The total lithium demand consists of both use in the blanket inventory and

burning on a continuing basis as to form tritium. Tritium is thus part of the fuel cycle. With the present state of knowledge of the technology, an order of magnitude estimate rather than exact values can only be made at this time. Figure 1 shows the production and demand of lithium as a function of time. This chart indicates the slow growth of the industry prior to World War II and shows the influence of wartime demands, especially in the peak production year of 1944. Projection of future production for conventional use is obtained by a linear regression based on the production rate of previous years. Production of lithium in 1968 was about 3000 short tons (2.7×10^6 Kg, Cummings, 1968). With an annual increase in the rate of about 5%, the lithium production in 2000 is estimated to be 1.2×10^7 Kg/year. When the requirement of fusion power in the U.S. reaches about 10^6 MW(e) beyond 2030, the quantity of natural lithium inventory required ranges from about $0.55 \times 10^7 \sim 4.7 \times 10^7$ Kg (Powell, 1975) for enriched solid CTR blankets to as high as 10^9 Kg for liquid lithium coolant blankets. Superimposing these quantities on the previous one for commercial use, the total quantity of lithium required lies between 4.3×10^7 and 10^9 Kg beyond the year 2030. Figure 1 gives the general trend of lithium production and demand for various time periods. Future projections of these curves may change with respect to the time scale but the shape of the curve should remain the same.

Table 1

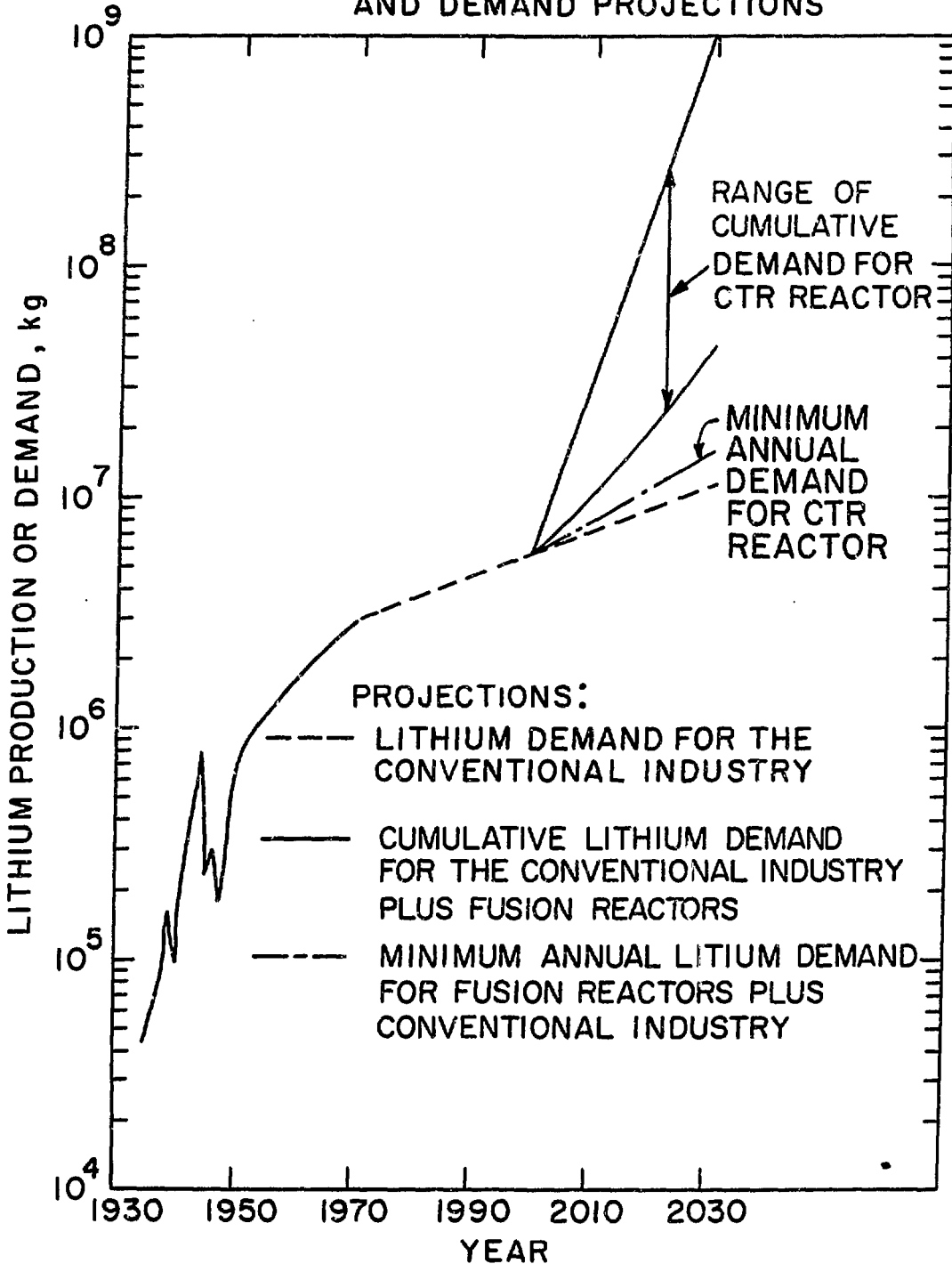
LITHIUM REQUIREMENT PER MEGAWATT FOR VARIOUS KINDS OF FUSION REACTORS INVENTORY

Reactor Type	ORMAK ^(a)	Tokamak ^(a)	θ Pinch ^(a)	ORNL ^(a) Laser	ILL DT ^(a) Mirror	BNL ^(b) Minimum Activity
Lithium Required per Megawatt Kg/Mw	804	454	377	325	182	5.5 ~ 46.8

a) Controlled Thermonuclear Research Division, Feb. 1973. Fusion Power: An Assessment of Ultimate Potential. WASH-1239, p. 20 and A-18.

b) Powell, J. R. Beryllium and Lithium Resource Requirements for Solid Blanket Designs for Fusion Reactors. BNL 20299, March 31, 1975.

FIG.1 LITHIUM PRODUCTION RATE AND DEMAND PROJECTIONS



Conventional lithium sources are minerals and brines.

In the U.S. most of the lithium minerals come from Kings Mountain, North Carolina. Mainly spodumene and some amblygonite are mined in North Carolina. South Dakota also has some reserves which consist of spodumene, amblygonite and lepidolite. Elemental composition of these minerals is shown in Table 2. Spodumene has the highest lithium composition as compared to the other minerals listed in the table and more than half of the Free World's output of lithium oxide comes from this source in 1963. Estimation of the total quantity of resources from these materials is about 0.89×10^8 Kg as can be seen in Table 2.

In order to produce more lithium and to reduce mining operations which rely on relatively expensive mining and conventional hydrometallurgical processing, brine has been investigated for an alternative source for lithium. Lithium has been found in brines in several places such as Silver Peak, Nevada; Great Salt Lake, Utah; Searles Lake, California; and Bonneville, Utah. Of these locations, lithium concentration is highest in Silver Peak, Nevada as can be seen in Table 2 (reference by PJB, 1966). Commercial practice has been carried out in Nevada, Utah, and California. Estimates of the content of two of the richest lithium brines are 3.45×10^9 Kgs in Silver Peak,

Table 2

MINERAL CONTENTS AND SOURCES OF LITHIUM
(weight percent)

Sources Mineral	Silver Peak, Nevada (a)	Great Salt Lake, Utah (a)	Sea Water (b)	Spodumene (c, d*)	Petalite (c, d*)	Lepidolite (c, d*)	Amblygonite (c, d*)
Sodium	7.5	7.0	1.08	0.36	0.68	0.50	0.88
Magnesium	0.06	0.8	0.13	0.60	--	--	--
Calcium	0.05	0.03	0.04	0.34	--	--	--
Lithium	0.04	0.006	0.000017	2.80	1.58	2.26	0.85
Potassium	1.0	0.4	0.04	0.60	0.17	10.18	--
Silicon	--	0.0004	0.0003	29.7	36.2	23.63	--
Aluminum	--	--	--	13.9	8.81	13.30	17.87
Iron	--	--	--	0.95	0.14	0.29	--
Sulfate	0.75	1.5	0.27	--	--	--	--
Chloride	11.7	14.0	1.94	--	--	--	--
Bromide	0.0	0.0	0.0004	--	--	--	--
Total Lithium Estimated (Kg)	3.45×10^9	5.91×10^8	2.5×10^{14}	6.89×10^8			

* All the metals are in oxide forms. Another major element in amblygonite is phosphorus.

(a) PJB, 1966, Nevada Brine Supports a Big New Lithium Plant, Chemical Engineering, August 15, p. 16.

(b) Riley, J. B. and Skirrow, G. 1965, Chemical Oceanography. Academic Press, p. 164.

(c) Cummings, A. M. 1968, Lithium in "Mineral Facts and Problems" by Staff of Bureau of Mines, 1970 ed. pgs. 1073-81.

(d) Mellor, J. W. 1946. A Comprehensive Treatise of Inorganic and Theoretical Chemistry, Vol. II, p. 425.

Nevada and 5.91×10^8 Kg in the Great Salt Lake in Utah as is shown in Table 2.

The total estimated supply of lithium from brine and mineral reserves is thus about 4.73×10^9 Kg, which comes close to the maximum cumulative quantity demanded for fusion reactors beyond 2030 estimated to be as high as 10^9 Kg. If there is any additional large demand for lithium such as for lithium sulfur batteries and for Li^7 as water conditioner in fission reactor, the reserves will not be sufficient to sustain a long term fusion economy. To remedy this situation, a large new lithium source of supply should be explored in conjunction with a reduction of fusion reactor lithium demand. In this report, seawater is examined as an alternate large source for Li. The concentration of lithium in seawater has been determined to be 170 ppb (Riley, 1964, 1965; Chow, 1962). Although the lithium concentration in the sea is very dilute, its quantity is tremendous--estimated to be about 2.5×10^{14} Kg. If annual requirement for lithium is a maximum of 4.32×10^6 Kg/yr after 2030 (Powell, 1975) for solid blanket or even about twenty times larger than the above quantity for liquid blanket the supply of lithium from the sea can last a million years or more. Thus the presence of unlimited

fuel resource as promised for a deuterium economy becomes possible. Obviously this is possible only if the technology for extraction of lithium from seawater becomes economically feasible.

The objective of the present paper is to outline a process for the extraction of lithium from seawater and to determine in a preliminary manner the mass, energy balance, and economics of such a process.

3. Process Concept for Extraction of Lithium from Seawater

Regardless of which process scheme is considered, the minimum theoretical energy requirement for extraction of lithium from seawater can be determined from the equation of minimum free energy change $\Delta F = RT \ln(\gamma N)$, where ΔF is computed to be 0.07 kwh(t)/gmLi.

Several possible routes for lithium extraction were considered mainly based on a study of the literature. The unit operations considered for the concentration of dilute species included adsorption, solvent extraction, ion exchange, evaporation, precipitation, and electrochemical separation. Ideally, it would be most advantageous to have a specific selective adsorbent for lithium. Although this is technically possible our literature survey did not reveal such an agent. As a result, preliminary calculations indicated that an extraction process involving concentration by solar evaporation followed by ion exchange and finally electrolytic separation may be a

reasonable process approach. This process has been studied to be a more economical one than a process using solar energy alone for salt separation.

Extraction of sodium chloride and magnesium from seawater by solar evaporation has been practiced on a commercial scale for many years (Shrier, 1952; Schambra, 1945). Extraction of uranium from seawater by an ion exchange method was proposed by Davies et al. (1964). The concentration of lithium in seawater lies between that of sodium and uranium. The application of solar evaporation alone can hardly produce pure lithium without subsequent chemical treatment because of its dilute concentration. Application of ion exchange beds alone will require a large quantity of ion exchange resins and therefore become uneconomical. Hence, a method of combination of solar evaporation and ion exchange is used for extraction of lithium from the sea. The separation and quantitative determination of lithium in seawater have been carried out by several investigators (Chow, 1962; Riley, 1964; Leont'eva, 1972) using ion exchange methods. Table 3 lists a survey of these methods. Strelow (1974) separated lithium from sodium, beryllium and many other elements by eluting lithium with 1 M nitric acid in 80% methanol from a column of AG50W-X8 sulphonated polystyrene cation-exchange resin. This method is similar to that of Riley (1964) and may be used for separation of lithium from seawater. The large engineering scale process design is based on the laboratory results of Riley (1964).

The plant can be located either by the seashore or on an offshore island. The ion exchange beds may be built in the strait so that power required to pump seawater to the beds may be eliminated.

A schematic flow diagram of the process is shown in Fig. 2. Sea water flows in the solar pond by tidal waves. Ponds can be built according to the topography of the seashore. The concentration ponds should be built at a higher elevation and the crystallization pond will be built at a lower elevation so that concentrated brine can flow from the concentration pond to crystallization pond by gravity. In the concentration areas, water is evaporated successively to different concentrations of lithium in ponds of various sizes. In the process of fractional crystallization of seawater, sodium chloride, calcium sulfate and magnesium chloride will precipitate first because of their much higher concentration and thus will reach their solubility limit first. Assuming the salts precipitated out in the order with calcium sulfate first, followed by sodium chloride and magnesium chloride, it is found out that when the seawater is concentrated 10^6 parts of original seawater upon evaporation, then lithium chloride will begin to precipitate out. The solar pond systems can be designed to be big enough such that 2 parts in 10^6 parts of water is left after solar evaporation. In this manner, the size and capital investment of the ion exchange bed can be greatly reduced.

The concentrated lithium brine is passed into the precleaned

Table 3.
LITERATURE ON SEPARATION AND DETERMINATION OF LITHIUM FROM SEAWATER

Author	Ocean or Sea	Li Concentration ($\mu\text{g}/\ell$)	Method of Separation	Method of Determination
(1) Marchand (1855)	English Channel	200		Gravimetric as Li_3PO_4
(2) Thomas and Thompson (1933)	North Sea	100	Precipitate Ca and Mg as carbonates, NaCl precipitated with alcohol or HCl. Residual Mg precipitated. Filtrate evaporated to dryness and residue extracted with alcohol	Visual flame spectrophotometry
(3) Goldschmidt et al. (1933)	North Sea	72		Spectrographic on sea salts
(4) Strock (1936)	North Sea	140		Spectrographic on dry salts
(5) Bardet et al. (1937)	North Atlantic	200	Li separated from NaCl by amyl alcohol extraction. Other elements removed by repeated precipitation and evaporation	Gravimetric as Li_2SO_4
(6) Ishibashi and Kurata (1939)	Pacific (Japanese Coastal Waters)	170	Concentrated by evaporation and elements removed by precipitation	Gravimetric
(7) Chow and Goldberg (1962)	Pacific	173	Sample enriched with ^6Li . Li separated by ion exchange and eluted with HCl	Isotope dilution
(8) Kappanna et al. (1962)	Indian (Coastal Waters)	160	Li + residual Mg precipitated as phosphate and weighed. Mg determined titrimetrically with EDTA	Gravimetric
(9) Riley et al. (1964)	All Oceans	183	Sample enriched with Li. Li separated by ion exchange and then eluted with HCl	Flame photometry
(10) Leont'eva et al. (1973)	High mineral solution	11000	ISM-1 ion-sieve cation exchange	Flame photometry

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ion exchange bed of Dowex 50-X16 (polymer beads of polystyrene crosslinked with 16% polyvinylbenzene). The characteristic of the Dowex resin is selective for exchange of its hydrogen ion with the cations in the seawater in the order of potassium, sodium, and lithium followed by magnesium. Sodium and potassium ions will be adsorbed first by the resins and then lithium ions will be adsorbed. After lithium ions are adsorbed, the remaining seawater will be concentrated in a smaller solar pond to concentrate the chloride ions in solution to a stronger hydrochloric acid. One can design the size of the bed to be big enough so that it can be operated 24 hours before the bed is saturated. In order to maintain continuous operations, a second bed is needed so that while one bed is functioning for the adsorption mode, the other bed can operate in the elution mode. Lithium ions are first eluted from the pregnant bed with 0.2-0.5 N hydrochloric acid. The eluted lithium chloride solution from the bed can flow in the evaporator to obtain concentrated lithium chloride or recycle back to the bed in order to elute more lithium ions. The lithium chloride then flows into an electrolyzer where lithium is electrolyzed. Hydrogen and chlorine from the electrolyzer react in a burner to form hydrogen chloride which is then dissolved in water from the evaporator to form dilute hydrochloric acid. The dilute hydrochloric acid is recycled back to the ion exchange bed to elute lithium ions. Other cations such as sodium, potassium ions, etc. will be eluted by concentrated hydrochloric

acid (8N) from the ion exchange bed after lithium ions are eluted out by dilute hydrochloric acid and before fresh seawater is passed in the bed. The eluted effluent is then passed back to the sea.

Evaporators used are triple effect backward feed evaporators. The assumed steam economy (total water evaporated/total steam supplied) is three. Boiling point elevation in each evaporator is neglected. Electrolyzer design follows closely the one described by Hader (1951) for electrolysis of lithium chloride.

4. Process Design and Economic Analysis

In the present design calculations, W gm/hr of lithium is taken as the production unit throughout and all the design quantities are based on this variable. Once W is defined, all other quantities may be computed.

The first major unit to design is the solar pond system. The rate of evaporation of water by solar energy is an important issue here. From a simple energy balance, one can take the heat required for evaporation to be supplied by solar radiation in accordance to the following equation

$$M\lambda = BA t \quad (1)$$

where λ is latent heat of water taken to be 1000 Btu/lb; B is the daily average solar energy received on the ground that varies from a few hundred to 2500 Btu/ft² (Lof, 1966); t is the time interval during which the seawater receives solar energy for evaporation;

A is the pond area in ft^2 ; M is the mass of water evaporated in lb. Validity of this equation can be examined from data of Silver Peak (PJB, 1966) which shows that 10^7 lb/yr of lithium carbonate is produced in a pond of 910 acres. Daily solar energy radiation received on the ground taken to be $1500 \text{ Btu}/\text{ft}^2$. In order to obtain the number of active days evaporation from about May to September each year (the period where abundant sunshine is received on ground in the West Coast), a correction factor of 0.5 is needed to validate the results of Silver Peak (PJB, 1966) in using Equation (1) which is a simple and good approximation for large complex solar pond systems. Hence, one can then apply Equation (1) for solar pond design for extraction of W gm/hr of lithium from seawater having an initial lithium concentration of 170 ppb. If we select a plant location in Southwest coast of the country with hourly solar energy intensity of $187.5 \text{ Btu}/\text{hr ft}^2$ and time of evaporation to be 3600 hr/yr, we can calculate the pond area to be $0.288 \times 10^5 \text{ W ft}^2$ in order to evaporate $2.36 \times 10^{10} \text{ W gm}/\text{yr}$ of seawater. For a production rate of lithium of $10^6 \text{ Kg}/\text{yr}$ which is sufficient for one 1000 MW (e) fusion reactor of ORMAK or one hundred 1000 MW(e) fusion reactors of BNL minimum activity blanket, the area of solar pond required is about 155 square miles. Utilization of waste heat of about $3 \times 10^9 \text{ Btu}/\text{hr}$ from a 1000 MW(e) fusion reactor for part of the heat supply for solar evaporation can also be considered. With the present design, it is found that using the waste heat for solar

evaporation can only be reduced by about 0.6 square miles or about 0.3% of the land calculated without using waste heat.

The concentration of cations initially in the seawater which will precipitate in salt form such as sodium chloride, calcium sulfate, magnesium carbonate, potassium chloride, etc. is about 0.0351 g/g seawater. When 2 parts of the initial 10^6 parts of seawater is left from evaporation (lithium chloride will begin to precipitate when 1 part of the initial 10^6 parts of seawater is left) 12.6 W gm/hr of bittern flows into the ion exchange bed for cation adsorptions. More than 99.9% of CaSO_4 , NaCl , MgCl_2 and KCl is precipitated in the crystallization ponds. The flow rate of bitterns that contain cations is 0.568 W gm-equivalent/hr. The capacity of Dowex-50 is 4.32 meq/gm and the design of the ion exchange bed is for 24 hour operation period before switching over to another bed. Then the total amount of resin required is 6320 W gm. The density of the resin is 0.802 gm/c.c. so the volume of each bed is 4.14×10^3 (W/N) c.c. where N is the number of beds. The ratio of height to diameter of bed is taken to be 15 (Dow 1958; Chow, 1962; Riley, 1964) so height and diameter of each bed are $93.5 (W/N)^{1/3}$ cm and $6.23 (W/N)^{1/3}$ cm respectively.

According to Riley and Tongudai (1964), 500 ml of 0.5 N HCL is used to elute 1.17 mg of lithium. Theoretically one equivalent of hydrogen ion can displace one equivalent of lithium so the hydrochloric acid can recycle 1176 times to elute lithium in the bed be-

fore it passes into the evaporator to drive off water from aqueous LiCl. The circulation load of hydrochloric acid is 1.5 W gal/min. Riley and Tonguadi reported that one liter of 4N HCl is used to elute other cations such as sodium, potassium, etc. from the bed. In the present operation, the concentrated hydrochloric acid required is less than that used by Riley and Tonguadi because more than 99.9% of the cations are precipitated. With this reduction of cations in the bittern, 25.6 W gm/hr of 4N hydrochloric acid is needed.

When all the hydrogen ions in 0.2 N hydrochloric acid are displaced by lithium ions in the the ion exchange bed, LiCl of 8.48 g/l flows into the evaporator at a rate of 746 W cc/hr.

To obtain a solid lithium chloride in the evaporator, 99.152% of water has to be evaporated. The evaporator type is a triple effect backward feed with a steam economy of 3. Process steam at 140 psia and 353°F is used to supply heat of evaporation of water. Using a heat transfer coefficient of 500 Btu/hr ft² o_F, one can estimate the heat transfer area of the evaporator to be 4.62 x 10⁻³ W square feet.

The electrolyzer used is similar to the one described by Hader (1951) except larger in scale. Cell of dimensions of 14' x 21' x 10.5' are used and its capacity is 161 lb/hr. Fourteen graphite anodes with 1.25 ft diameter and 21 ft long are supported from above the cell and extend downward into the electrolyte bath. The cathode is made of steel. Operating conditions would be the same as in a

Table 4

**EXTRACTION OF LITHIUM FROM SEAWATER
SUMMARY OF DIMENSIONS AND NUMBERS OF MAJOR PIECES OF EQUIPMENT.**

Equipments	Ion Exchange Bed	Pumps	Evaporator	Electrolyzer	Solar Pond
Dimensions	Height (h) $= 3.07 (W/N)^{1/3}$ Diameter (D) $= h/15$	7000 gal/min	Total Area $= 4.62 \times 10^{-3} W \text{ ft}^2$	21 ft x 14 ft x 10.5 ft	Area = $\frac{2 \text{ m}\lambda}{\text{Bt}}$
Number of Units (N)	$N = (153.5/h)^3$	$N = 2.14 \times 10^{-4} W$	N = 3	$N = \frac{W}{454 \times 161}$	155 mi^2 $12.4 \text{ mi} \times 12.4 \text{ mi}$
Values are given for W = $1.25 \times 10^5 \text{ g/hr}$	N = 17 when h = 60 ft D = 4 ft N = 5 when h = 90 ft D = 6 ft	27	645 ft ² each	2	

conventional cell (Hader, 1951). Table 4 shows a summary of the dimensions and number of major units. The area of the solar pond is a significant factor in the present process. Table 5 shows the areas of ponds required for various production rates of lithium based on Equation (1).

An important aspect of the process is the energy requirement. Mechanical energy is required to transport bittern and hydrochloric acid between the ion exchange bed and other pieces of equipment. The mechanical energy equation for fluid transport in the present system is:

$$\frac{g}{g_c} \Delta h + \frac{\Delta u^2}{2g_c} + \frac{2fLu^2}{g_c D} + W_s = 0 \quad (2)$$

where the first term is for potential energy, the second term is for kinetic energy, the third term is frictional losses in the pipe line, with Fanning friction factor f , length of pipe L , diameter of pipe D and the fourth term is the pumping power required with the pumping efficiency 80%. Writing the velocity term in terms of the mass flow rate of liquid and the diameter of pipe, one can rewrite Equation (2) as follows:

$$\frac{g}{g_c} \Delta h + \frac{8G^2}{g_{cp}^2 D^4} + \frac{32f L G^2}{g_{cp}^2 D^5} + W_s = 0 \quad (3)$$

By substituting the mass flow rate for bittern (3.5×10^{-3} W lb/hr), 0.5 N HCl (6.3 W lb/hr), 4N HCl (5.64×10^{-2} W lb/hr), height of ion exchange bed and length of transporting line which is taken

Table 5

EXTRACTION OF LITHIUM FROM SEAWATER.
SOLAR POND AREA AS A FUNCTION OF LITHIUM
PRODUCTION RATE.

Lithium Production Rate (Kg/yr)	Solar Pond Area (Square Miles)
10^4	1.55
10^5	15.5
10^6	155

Note: for higher production rate, one can have plants located in several sites so that the requirement for solar pond area will not be concentrated in one location.

7.1 times of the bed height, one can obtain the pumping power required in terms of kwh(e)/lb Li as:

$$\frac{0.35 \times 10^{-9} W}{D^4} + 1.35 \times 10^{-4} h + 0.61 \times 10^{-11} \frac{W^2 h}{D^5}$$

The thermal energy required in the evaporation is 73.1 kwh(t)/lb Li. With 80% cell efficiency, energy required in the electrolyzer is 8.15 kwh(e)/lb Li. So total energy required for extraction of lithium from seawater by the present process in terms of kwh(e)/lb Li is then:

$$\frac{0.35 \times 10^{-9} W}{D^4} + 1.35 \times 10^{-4} h + 0.61 \times 10^{-11} \frac{W^2 h}{D^5} + 37.39$$

Table 6 shows a summary of energy requirements calculated from the above expression for various lithium production rates, pipe sizes for liquid transport and heights of ion exchange bed. When lithium production rate is less than 10^5 Kg/yr, the energy requirement for the present process is mainly for thermal energy in the evaporation and electrical energy for the electrolyzer. At higher production rate, pumping energy becomes more important. When lithium production rate is less than 10^6 Kg/yr, energy requirement for lithium extraction is less than 0.2 kwh(e)/gm Li. Energy requirement increases with increase in lithium production rate and height of ion exchange bed mainly due to increase in pumping power for liquid transport in the pipe line. However, increased pipe size will decrease energy requirements, as can be seen in a decrease from 1.667 to 0.719 kwh(e)/gm

Table 6

SUMMARY OF ENERGY REQUIREMENT FOR LITHIUM EXTRACTION FROM SEAWATER AT VARIOUS LITHIUM PRODUCTION RATES, PIPE SIZE FOR LIQUID TRANSPORT AND HEIGHT OF ION EXCHANGE BED.

Lithium Production Rate Kg/yr	Diameter of Pipe	Height of Ion Exchange Bed	Energy Requirement for Li Production	
	D(ft)	h(ft)	kwh(e)/gm	(kwh(e)/lb)
10 ⁴	1	60	0.082	(37.39)
	1	90	0.082	(37.39)
	2	60	0.082	(37.39)
10 ⁵	1	60	0.083	(37.46)
	1	90	0.165	(37.50)
	2	60	0.082	(37.39)
10 ⁶	1	60	0.098	(44.46)
	1	90	0.106	(48.00)
	2	60	0.083	(37.61)
10 ⁷	1	60	1.642	(745.39)
	1	90	2.422	(1099.39)
	2	60	0.131	(59.52)
10 ⁸	2.5	60	1.667	(761.5)
	2.5	90	2.460	(1123.6)
	3	60	0.719	(328.4)

*Energy requirements include pumping energy, evaporator energy, and energy for electrolysis.

for pipe size increase from 2.5 to 3.0 foot diameter at lithium production rates of 10^8 Kg/yr and bed height of 60 feet. Even using the most energy intensive case in our study (2.46 kwh(e)/gm) for production of lithium of 10^8 Kg/yr which is sufficient to build 124 ORMAK or 10^4 BNL minimum activity blanket fusion reactors of 1000 Mw(e), one can see that the present process is still an energy efficient one compared to the minimum natural lithium energy content estimated by Lee (1960) for fusion reactor as 3400 kwh(e)/gm Li.

A preliminary economic assignment of the process has also been studied. A solar pond is made of a dike surrounding an area holding seawater and can be constructed at a negligible cost compared to the other major items such as equipments and ion exchange beds. The cost of the pump is obtained from Peters (1968, p. 466). The cost of the electrolyzer is evaluated from its basic material cost such as steel and graphite (Cummings, p. 1032). The cost of the evaporator and burner for HCl is obtained from Popper (1970, p. 145 and p. 87). Table 7 lists the capital investment of the present process for extraction of lithium from seawater in terms of W gm/hr of lithium production rate in 1970 dollars. Results of the capital investment for three different lithium production rates (10^4 - 10^6 Kg/yr) are exhibited in Table 8. Table 9 gives the production cost of the process. The cost of steam is reasonably taken to be 0.249¢/1000 gm (\$1.15/1000 lb) (Peters, p. 772) or 0.07¢/gm Li and a small cost is taken for HCl in the recycling elution process.

Table 7

CAPITAL INVESTMENT FOR A PLANT FOR THE EXTRACTION OF LITHIUM FROM SEAWATER IN TERMS OF W gm/hr LITHIUM PRODUCTION RATE.

<u>Item</u>	<u>Capital Cost (\$)</u>
(1) Resin Beds	70W
Pumps	221.9W ^{0.489}
Evaporator	2.1W ^{0.8}
Electrolyzer	0.3W
Burner	184.6W ^{0.85}
(2) Land for solar pond 4.6% of item (1) ^(a)	3.23W + 8.49W ^{0.85} + 10.2W ^{0.489} + 0.1W ^{0.8}
(3) Piping 29% of item (1) ^(a)	20.4W + 53.5W ^{0.85} + 64.4W ^{0.489} + 0.6W ^{0.8}
(4) Service facilities 56% of item (1) ^(a)	39.4W + 103.4W ^{0.85} + 124.3W ^{0.489} + 1.2W ^{0.8}
(5) Unlisted equipment & misc. 10% of above ^(b)	13W + 34.2W ^{0.85} + 41.1W ^{0.489} + 0.4W ^{0.8}
(6) Installation of equipments 35% of above ^(a)	$\frac{45.5W + 119.7W^{0.85} + 143.9W^{0.489} + 1.4W^{0.8}}{191.9W + 503.9W^{0.85} + 605.8W^{0.489} + 5.8W^{0.8}}$
(7) Site preparations, buildings 20% of above ^(b)	38.3W + 101W ^{0.85} + 121.2W ^{0.489} + 1.2W ^{0.8}
(8) Electrical & instrumentation 20% of above ^(b)	38.3W + 101W ^{0.85} + 121.2W ^{0.489} + 1.2W ^{0.8}
Subtotal	268.5W + 705.9W ^{0.85} + 848.2W ^{0.489} + 8.2W ^{0.8}
(9) Total, 2 times ^(c) to include engineering, construction overhead and contingency	537W + 1411.8W ^{0.85} + 1696.4W ^{0.489} + 16.4W ^{0.8}

^{a)} Peters, M. S., Timmerhaus, K. W. 1968 "Plant Design and Economics for Chemical Engineers", 2nd ed. McGraw-Hill, p. 104.

^{b)} Harrington, F. E. et al., 1966, ORNL Central Files No. 66-2-57, p. 36.

^{c)} Page, J. S. Estimators Manual for Equipment and Installation Cost, p. 124-27.

Table 7

CAPITAL INVESTMENT FOR A PLANT FOR THE EXTRACTION OF LITHIUM FROM SEAWATER IN TERMS OF W gm/hr LITHIUM PRODUCTION RATE.

<u>Item</u>	<u>Capital Cost (\$)</u>
(1) Resin Beds	70W
Pumps	221.9W ^{0.489}
Evaporator	2.1W ^{0.8}
Electrolyzer	0.3W
Burner	184.6W ^{0.85}
(2) Land for solar pond 4.6% of item (1) ^(s)	3.23W + 8.49W ^{0.85} + 10.2W ^{0.489} + 0.1W ^{0.8}
(3) Piping 29% of item (1) ^(a)	20.4W + 53.5W ^{0.85} + 64.4W ^{0.489} + 0.6W ^{0.8}
(4) Service facilities 56% of item (1) ^(a)	39.4W + 103.4W ^{0.85} + 124.3W ^{0.489} + 1.2W ^{0.8}
(5) Unlisted equipment & misc. 10% of above ^(b)	13W + 34.2W ^{0.85} + 41.1W ^{0.489} + 0.4W ^{0.8}
(6) Installation of equipments 35% of above ^(a)	$\frac{45.5W + 119.7W^{0.85} + 143.9W^{0.489} + 1.4W^{0.8}}{191.9W + 503.9W^{0.85} + 605.8W^{0.489} + 5.8W^{0.8}}$
(7) Site preparations, buildings 20% of above ^(b)	38.3W + 101W ^{0.85} + 121.2W ^{0.489} + 1.2W ^{0.8}
(8) Electrical & instrumentation 20% of above ^(b)	38.3W + 101W ^{0.85} + 121.2W ^{0.489} + 1.2W ^{0.8}
Subtotal	268.5W + 705.9W ^{0.85} + 848.2W ^{0.489} + 8.2W ^{0.8}
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a) Peters, M. S., Timmerhaus, K. W. 1968 "Plant Design and Economics for Chemical Engineers", 2nd ed. McGraw-Hill, p. 104.

b) Harrington, F. E. et al., 1966, ORNL Central Files No. 66-2-57, p. 36.

c) Page, J. S. Estimators Manual for Equipment and Installation Cost, p. 124-27.

Table 8

CAPITAL INVESTMENT FOR PLANTS FOR THE EXTRACTION OF LITHIUM FROM SEAWATER

Capacity range 10^4 - 10^6 Kg/yr plants (1974 dollars)

Item	Capital Cost (\$10 ⁶)			Percentage of Total		
	10 ⁴ Kg/yr	10 ⁵ Kg/yr	10 ⁶ Kg/yr	10 ⁴ Kg/yr	10 ⁵ Kg/yr	10 ⁶ Kg/yr
(1) Resin Beds	0.09	0.88	8.75	7.2	8.4	9.4
Pumps	0.00	0.01	0.04	0.2	0.1	0.0
Evaporators	0.00	0.00	0.02	0.0	0.0	0.0
Electrolyzers	0.00	0.00	0.04	0.0	0.0	0.0
Burner	0.07	0.46	3.31	5.4	4.5	3.5
(2) Land for solar ponds	0.00	0.06	0.56	0.5	0.6	0.6
(3) Piping	0.04	0.39	3.52	3.7	3.8	3.8
(4) Service facilities	0.09	0.76	6.80	7.2	7.3	7.3
(5) Unlisted equipment & misc.	0.03	0.26	2.31	2.5	2.5	2.5
(6) Installation of equipments	0.11	0.90	8.07	8.9	8.6	8.6
(7) Site preparations, buildings	0.09	0.74	6.68	7.2	7.1	7.1
(8) Electrical & instrumentation	0.09	0.74	6.68	7.2	7.1	7.1
Subtotal	0.60	5.13	46.78	50.0	50.0	50.0
(9) Eng., Const. Overhead & Contingency	0.60	5.13	46.78	50.0	50.0	50.0
Total	1.21	10.43	93.56	100.0	100.0	100.0

Table 9

PRODUCTION COST FOR EXTRACTION OF LITHIUM FROM SEAWATER IN TERMS OF W gm/hr LITHIUM PRODUCTION RATE
(1974 dollars)

Items	Production Cost cents/gm Li	Cents/gm Li				Percentage of Total			
		10^4 Kg/yr	10^5 Kg/yr	10^6 Kg/yr	10^7 Kg/yr	10^4 Kg/yr	10^5 Kg/yr	10^6 Kg/yr	10^7 Kg/yr
Lithium Production Rate									
Yearly Charge 13% ^(a)	$0.85 + 2.25W^{-.15} +$ $2.71W^{-.511} + 0.03W^{-.2}$	1.70	1.42	1.25	1.12	54.0	53.4	53.2	51.4
Electrical En- ergy Cost (for pumping and electrolysis) 1.5¢/kwh(e)		0.03	0.03	0.04	0.05	0.9	1.1	1.7	2.31
Steam Cost ¢0.249/1000 gm	0.07	0.07	0.07	0.07	0.07	2.6	2.6	3.0	3.21
Raw Material	0	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.00
Chemical (HCl)	0.07	0.07	0.07	0.07	0.07	2.2	2.6	3.0	3.21
Maintenance, labor, etc. 10% ^(b)	$0.66 + 1.73W^{-.15} + 2.08W^{-.51}$ $0.02W^{-.2}$	1.31	1.10	0.96	0.87	41.6	41.4	40.8	39.9
Total	$1.65 + 3.93W^{-.15} + 4.6W^{-.5}$ $0.05W^{-2}$	3.18	2.69	2.34	2.18	100.0	100.0	100.0	

(a) Harrington, F. E. et al., 1966, ORNL Central Files No. 66-2-57, p. 37.

(b) Kunin, R., 1958, Ion Exchange Resins, 2nd. ed. Wiley & Sons, p. 396.

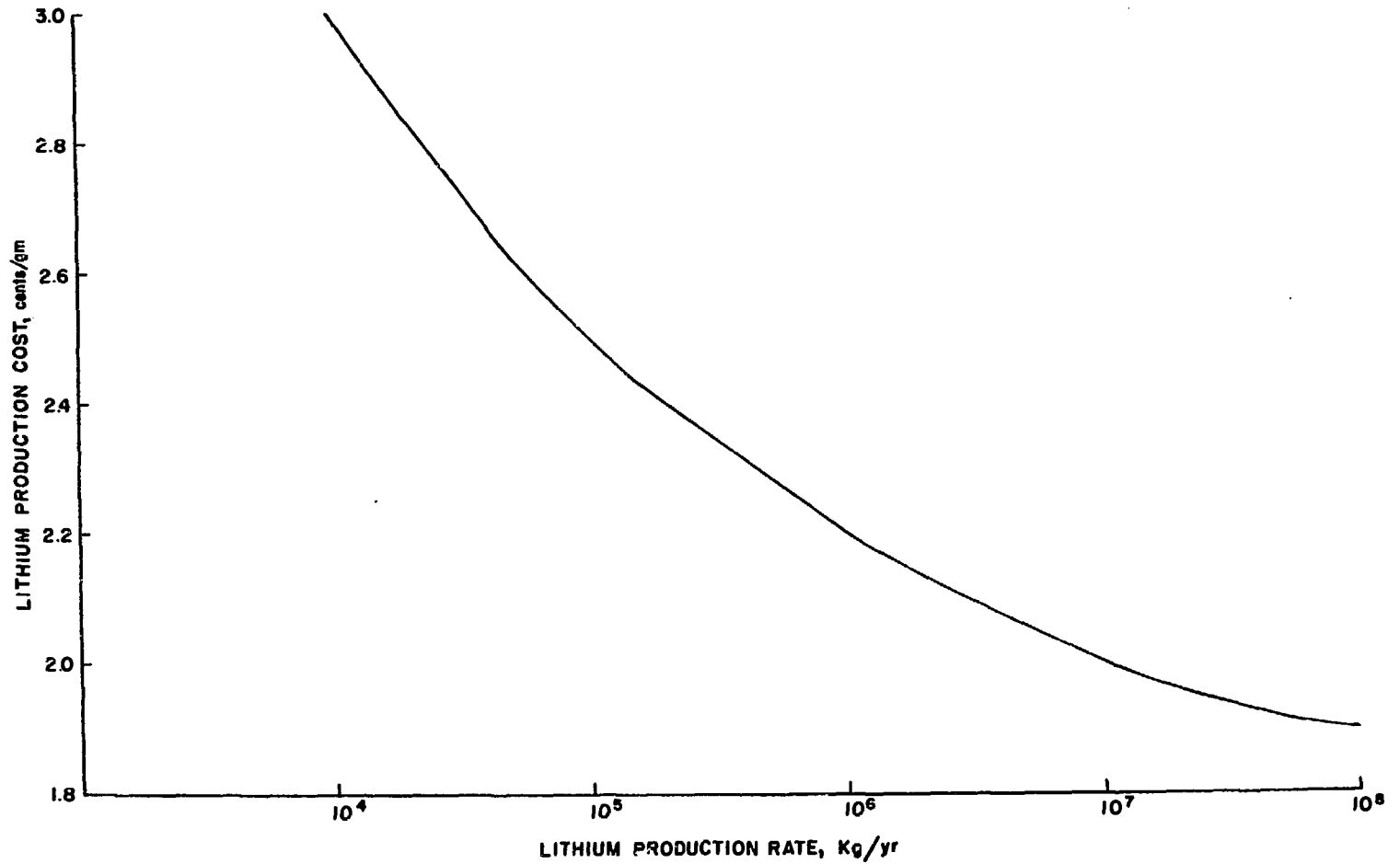
100

Table 8 and Figure 3 shows the lithium production cost versus lithium production rate. The production costs range from 2.2¢ to 3.2¢/gm. It is seen that the production cost (1974 value) is competitive with the cost of lithium at 2 cents/gm (Holdren, 1971). The costs are somewhat higher than the selling price of lithium at 2¢/gm (Holdren, 1971). In terms of use in fusion reactors the per kwh(e) cost is no more than 0.01 mill/Kwh(e) which thus insures a negligible cost. The main thing is the resource availability which is insured by the sea.

Conclusion

A process for the separation of lithium from seawater is designed based on solar evaporation and ion exchange sorption/desorption followed by electrolytic recovery for metal. The preliminary analysis shows that the process appears to be technically feasible. Uncertainties exist in the practical operation of large ponds. The energy requirement for lithium extraction by this process can be as low as 0.082 to as high as 2.46 kwh(e)/g Li depending on lithium production rate. Compared to the equivalent minimum nuclear energy content of natural lithium of 3400 kwh(e)/gm, the energy requirement for this process is relatively small. A preliminary economic analysis shows that the production cost of lithium for the present process is in the range of 2.2 to 3.2 cents/gm (1974 values) which is slightly above present selling price of about 2.0¢/gm from conventional mineral resources. The point is that

Fig. 3. LITHIUM PRODUCTION COST VERSUS LITHIUM PRODUCTION RATE



it should be possible to insure an unlimited resource for lithium for the long term fusion economy at a reasonable cost. To remove the uncertainties in the process technology it is recommended that a phase study of the salts in the sea be undertaken to determine the liquid-solid equilibrium during solar evaporation. It is further recommended that a laboratory search for a highly selective absorbent or adsorbent for extraction of lithium from seawater be undertaken on a continuing experimental effort so as to insure the technology when it will be needed.

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