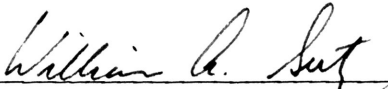EFFICIENCY OF HETEROSALINE VAPOR PUMPS

by

Jonathan Fadely

Marine Sciences

Submitted in Partial Fulfillment of the Requirements of the
University Undergraduate Fellows Program

1981-1982

Approved by:

_____
Dr. William A. Seitz

ABSTRACT

Of the known sources of ocean energy, salinity gradients have the most potential. These gradients are found naturally in estuarine environments, but can be artificially produced, given a salt source, such as a hypersaline lake or salt dome. The heterosaline vapor pump is the most promising of the proposed methods of utilizing this energy, as it eliminates the need for the expensive membranes common to the other methods. The vapor pump operates on the difference in vapor pressures between salt and fresh waters. This difference is the driving force of the pump, and varies with both salinity gradient and temperature. It serves to define the maximum efficiency of the pump :

$$E = \frac{p_O - p'}{p_O}$$

where (p_O) is the vapor pressure of the fresh or hypotonic solution, and (p') is the depressed vapor pressure of the salt or hypertonic solution. Experimental results indicate that efficiency is independent of temperature, but increases with an increased salinity gradient. Higher efficiencies are obtained by using two salt solutions, rather than freshwater and a salt solution to construct a given gradient.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

—

LIST OF FIGURES

INTRODUCTION

Man has employed the sea in many ways throughout history; today he is still discovering unknown resources, and extending the use of already-familiar ones. Research in ocean energy is a prime example; there are a variety of sources, some tried and proven, others just recently proposed.

At present, there are three general classes of ocean energy: kinematic, thermal gradient, and salinity gradient. Relative energy densities are given in Table 1, expressed as equivalent meters of water head.

Table 1: Ocean Energy Sources (Schmitt & Wick 1978)

Source	Energy Density(m)
Salinity Gradient	240
Thermal Gradient	210
Tides	10
Waves	1.5
Currents	0.05

Kinematic sources include tides, currents, and waves. In general, they are converted to usable energy by mechanical means. Thermal gradients, established between cold, deep waters and warm, surface waters, can drive low-power heat engines to produce energy. This is the basis of the Ocean Thermal Energy Conversion (OTEC) project. Salinity gradients, which are changes in the concentrations of dissolved salts between two water masses, are perhaps the least researched, yet most promising of all sources to date. There are a variety of proposed means of salt energy conversion, but the three most common are reverse electrodialysis, pressure-

---

The format of this paper is based on articles published in the Marine Technological Society Journal.

retarded osmosis, and heterosaline vapor expansion (more commonly termed reverse vapor compression). Of these three, the latter is most practical, as the former two require the use of expensive, fragile semi-permeable membranes. The purpose of this thesis is to examine the limiting factors of power output of a reverse vapor compression engine, or heterosaline vapor pump, and to determine what constraints, if any, there might be on maximum pump efficiency.

LITERATURE REVIEW

Lee has approached the topic of semi-permeable membranes for use in the reverse electrodialysis and pressure-retarded osmosis methods (1980). Of the proposed extraction methods, pressure-retarded osmosis has been discussed in the most detail, perhaps because it is the most obvious (Norman 1974; Loeb 1975). The heterosaline vapor expansion method was first proposed by Wick and Isaacs (1976); a full report was published later (Olsson, et al. 1979). Subsequently, questions were raised about the effective cost of salt energy, and the impact its conversion would have on the environment (Williams 1979; Wick & Isaacs 1979).

There are several reviews of the status of ocean energy in print (Schmitt & Wick 1978; Wick 1979). In one review, questions are raised about fundamental limiting constraints on the efficiency of each process, and, as one of the authors wrote (Isaacs & Schmitt 1980):

    A new analysis of the nature of electrolytic solutions and
    the potential for power generation from this immense source
    is needed. The outlook at present is moderately encouraging.

SALINITY GRADIENTS

Definition

A salinity gradient, as defined above, is a change in salinity between two water masses. The use of the term gradient may be a little misleading, as the phenomena observed of such a change require adjacent water masses, and are therefore essentially independent of distance. True gradients--changes in salinity with respect to changes in space-- do occur in nature, and the distances involved will have a bearing on the cost-effectiveness of any energy extraction mechanism. However, the term salinity gradient, for the purposes of this thesis, shall refer to the condition that exists between heterosaline solutions; simply put, a net change in salinity.

Sources

There are a variety of sources for salinity gradients, or more essentially, sources of salts. Estuaries have in the past received quite a bit of attention, because of their natural juxtaposition of salt and fresh water. There is some concern, however, about the environmental impact of altering the natural mixing process, as would occur during the operation of a heterosaline power plant (Williams 1979). Additionally, power outputs from such plants would be relatively low, because of the low salinities, and corresponding small gradients found in these areas.

The alternative is to plan power plants around salt deposits. With a source of salts, the necessary solutions may be artificially produced, then used and even recycled. Some proposed sources of brine include hypersaline lakes and seas, such as the Red Sea, or Great Salt Lake

(Loeb 1975). Solid salt could be obtained from salt flats along the coast. It is presently mined from subterranean deposits, such as the salt domes in Michigan and Texas. Ironically, these domes are often associated with petroleum deposits. Theoretical predictions indicate that more energy may potentially be available from the salt in these domes, than from the oil pockets in them. For example, it has been esti- mated that a high oil-yield dome, specifically the Humble dome, in Harris, Texas, will produce 24,000 MW-years of oil energy; in contrast, it could produce up to 350,000 MW-years of salt energy (Wick & Isaacs 1978).

Characteristics

There are several characteristics of salinity gradients which make them viable energy sources. The first, and perhaps most readily apparent, is the osmotic potential, or pressure. Two others, the vapor pressure differential, and the enthalpy of mixing, are utilized specifically in the heterosaline vapor expansion method.

The vapor pressure differential occurs because of the difference in vapor pressures of fresh and salt water. The salt solution has a lower vapor pressure, because of the displacement of water molecules by salt ions. The fresh water therefore evaporates faster, and builds up a vapor pressure head, as long as the salinity gradient is maintained.

The enthalpy of mixing salt and fresh water, generated by the dilution of the salt ions, is not readily observed in nature because of the high heat capacity of water (Schmitt & Wick 1978). However, at the low pressures under which the heterosaline vapor pump operates, this energy (approximately 9.2 cal/g for a mix of distilled water and saturated brine) is significant (Olsson, et al. 1979). In essence, the salt solution may

be regarded as a consumable fuel source.

In summary, the conversion of salinity gradient energy by the hetero-saline vapor expansion method operates on the principle of competitive evaporation between salt and fresh, or hyper- and hypotonic solutions. The driving force is the vapor pressure differential, and the potential energy of the system is the enthalpy of mixing the given solutions.

HETEROSALINE VAPOR PUMPS

Construction

The ideal heterosaline vapor pump would maximize each of the above characteristics, while remaining easy and cheap to construct and maintain. Designs may vary, but six basic elements are common to all pumps (Fig. 1). These are the solution containers, evaporative surface, vapor passage, condensing surface, heat exchanger, and gauge or power take-off.

In simpler models, the evaporative and condensing surfaces are the surfaces of the fresh and salt solutions, and the fresh and salt sides of the heat exchanger. This exchanger is generally a simple metal plate or sheet, omni-directional in flow. For the purposes of research, a gauge is interposed in the vapor passage. The gauge used in this study was an oil manometer, connected in parallel with a cross-connect bleed valve. In practical applications, this gauge would be replaced by a power take-off mechanism, such as a turbine.

Generally, materials for the pump itself can be found in any good local hardware store. PVC pipes and fittings are very satisfactory, and have been used with some success in the past (Olsson, et al. 1979). Sealants should be chosen carefully and tested under operating conditions;

POWER TAKE-OFF

VAPOR PASSAGE

HEAT EXCHANGER
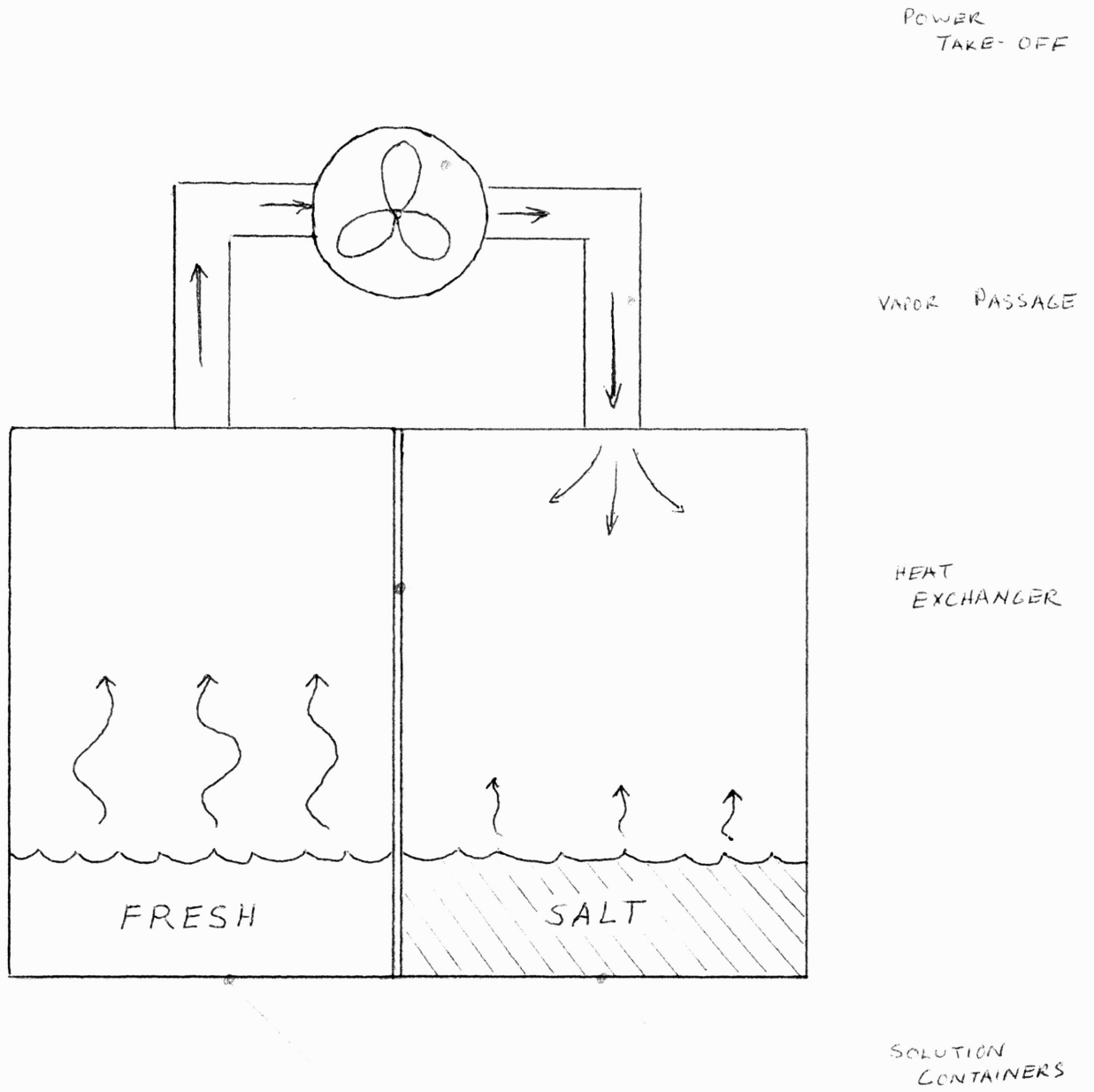
FRESH

SALT

SOLUTION CONTAINERS

Fig. 1: Heterosaline Vapor Pump

those which are water- and air-tight under ambient conditions may dissolve or deteriorate in the low-pressure, saturated environment of the pump.

Operation

As stated above, the pump operates on the principle of competitive evaporation. Because of its higher vapor pressure, fresh or less salty water will evaporate faster than more salty water. This differential rate may be enhanced by lowering the ambient pressure in the chambers. Initially, evaporation is quite rapid, but it slows down as the chambers are saturated with water vapor. If both solutions were losing and regaining vapor at the same rate, the system would be at equilibrium. Because of the difference in vapor pressures, however, the water vapor is absorbed by the salt solution. Two effects are the result of this absorption.

First, the humidity of the chambers is decreased, permitting more water to evaporate. Second, the addition of pure water to the salt solution generates the enthalpy of dilution, which ideally is transferred to the fresh solution through the heat exchanger, to enhance evaporation.

As time progresses, the salt solution will become more dilute, and eventually the system approaches equilibrium, as the vapor pressure of the diluted salt solution nears that of the fresh solution, and the enthalpy of mixing approaches zero (Fig. 2). This approach to equilibrium is asymptotic with respect to time for a fresh-salt system; the salt solution will never be as dilute as the fresh. In a system of two salt solutions of differing concentrations, this time to equilibrium is finite. At equilibrium, the concentrations of the two solutions would be equal, the hypotonic solution having been concentrated, and the hypertonic, diluted.
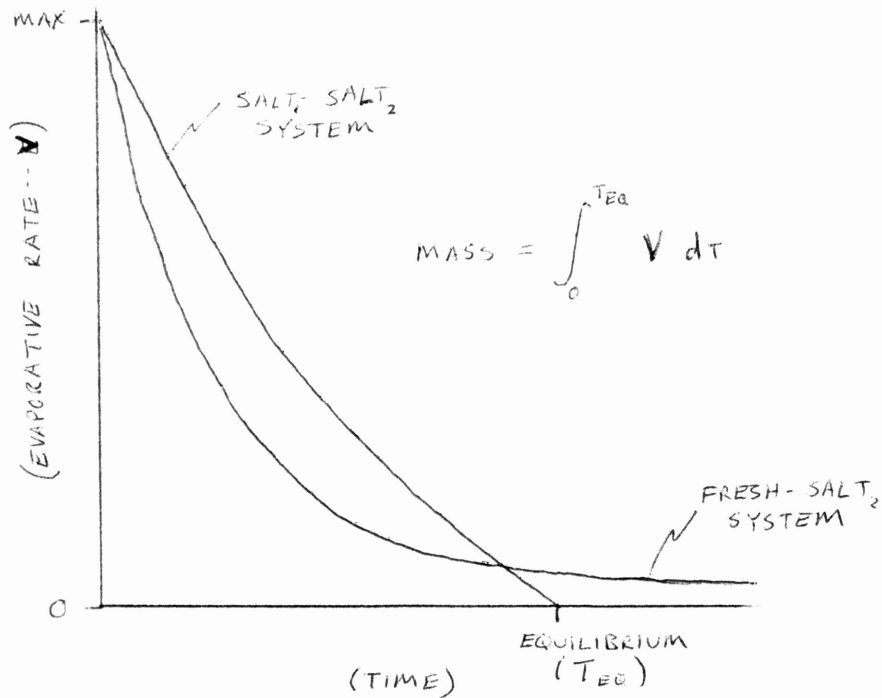
Fig. 2: System Equilibria

EFFICIENCY

Definition

Before studying efficiency, or the effective use of total available energy, that energy must first be defined. Olsson, et al. (1979) normalized their experimental measurements to 9.2 cal/g, the theoretical enthalpy of mixing brine and fresh water. Subsequently, they reported that near-100% efficiency levels were possible. These high levels, however, are an a priori result of measured mass transfer, and essentially reflect the efficiency of their particular pump model's heat exchanger.

While the energy of the system is indeed the enthalpy of mixing, the pump's efficiency should be based on potential rather than actual mass

transfer. Referring to the equilibria graph (Fig. 2), this potential transfer is the integral area under the appropriate curve. This area is a function of the maximum vapor pressure of the system--the vapor pressure of the fresh or hypotonic solution.

Mass Transfer Rate

The actual mass transfer rate of the pump is directly related to the net, or competitive evaporative rate. This evaporative rate, in turn, is affected by several factors: wetted surface area, humidity, agitation or surface turbulence, ambient pressure, and solution vapor pressure.

For the purposes of this study, the majority of these factors were equal for both solutions. Surface area was essentially the same throughout each set of experiments. The space in the test chambers was saturated with water vapor during an initialization period before each experiment. Surface turbulence was internally generated by boiling activity, and both chambers were evacuated. The differences noted in evaporative rates, therefore, were due to differences in the vapor pressures of each solution, which depend on solute concentration and temperature.

In general, the more concentrated the solution is, the lower the vapor pressure will be, while the higher the temperature is, the higher the vapor pressure will be. These are not linear correlations, however. In the case of solute concentration, the vapor pressure of the salt soution is less than would be expected for an ideal solvent (Fig. 3). This depression increases as salt concentration increases. As temperature is increased, vapor pressure increases in exponential proportion to the temperature (Fig. 4).
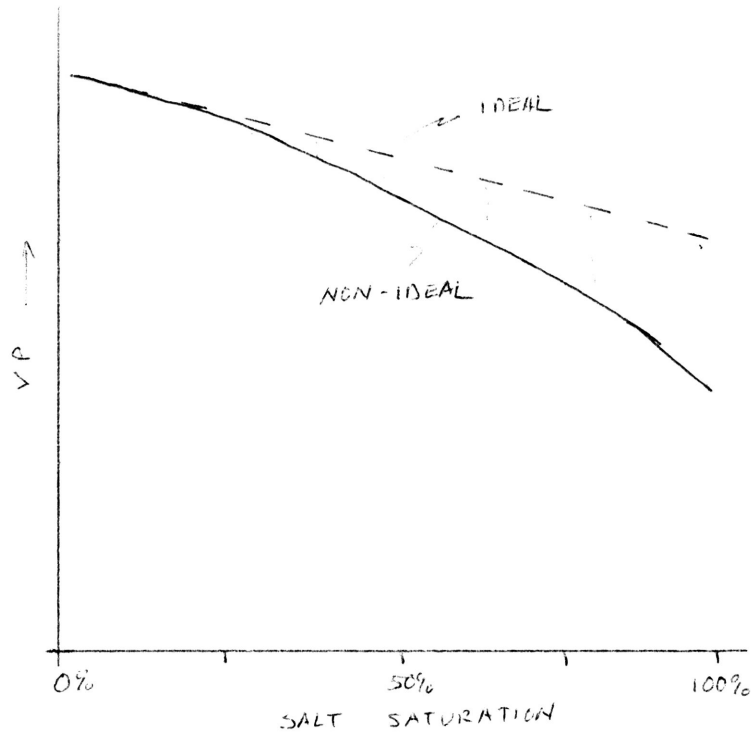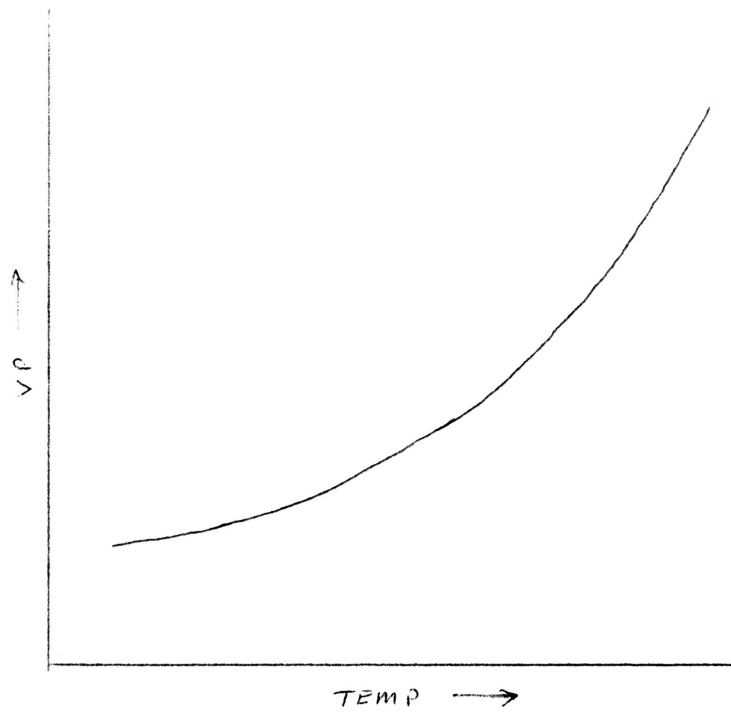
Fig. 3

Fig. 4

RESULTS

To verify these relations, a series of vapor pressure experiments were run, in which both the salinity gradient and the ambient temperature were varied. Details of the experimental materials and methods may be found in the Appendix. Two sets of data were generated from this research: vapor pressure differences, and power outputs. The vapor pressure data are based on initial pressure differences after a unit period of time. The power data are based on measurements of the rate of pressure change in the given volume of the saturated system. Both sets are relative, rather than absolute; their value lies not in establishing operating maxima, but rather in defining correlations, as shown in Figures 5-8.

Because of technical problems associated with natural sea-water (Olsson, et al. 1979), pure sodium chloride solutions were used in these experiments. Sea- and salt-water have similar characteristics; the interpretations based on the latter should apply to the former.

DISCUSSION

The data in general follow the theoretical predictions (Figs. 3, 4). There is a deviation in the $40^{\circ}C$ range of the vapor pressure difference (fig. 6), but this is most probably due to experimental error, given the trend of the data up to that point. In these graphs, plotted points reflect the adjusted experimental data, and heavy curves indicate the general trends of the points.

The changes observed in vapor pressure with respect to salinity gradients (Fig. 5) are depicted in contrast to the expected changes in
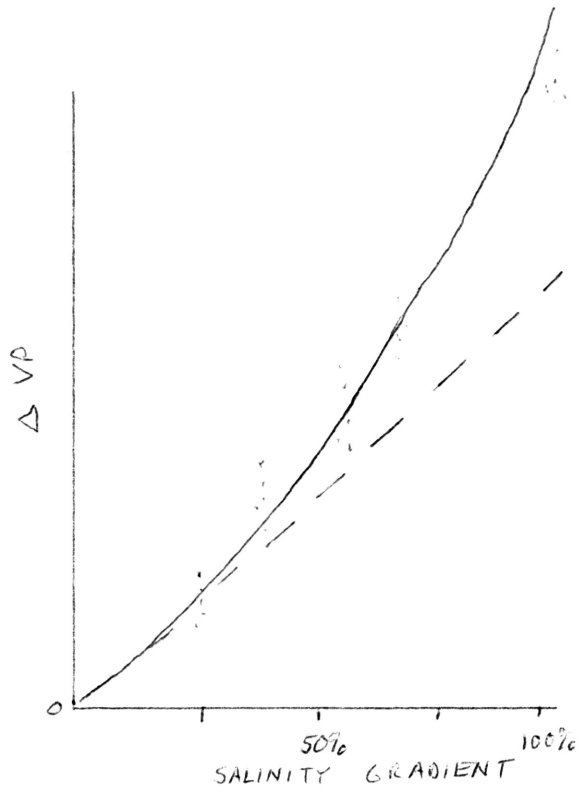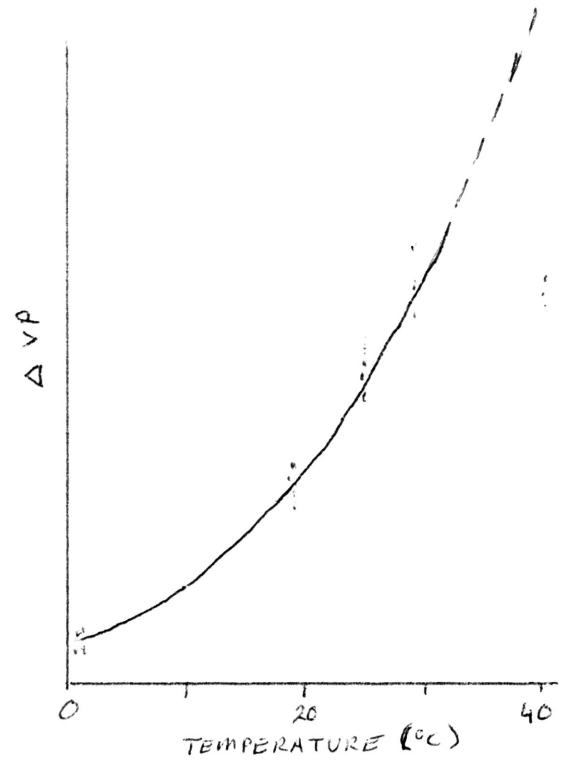
ΔVP

50% SALINITY GRADIENT 100%

Fig. 5

ΔVP

0 20 40
TEMPERATURE (°C)

Fig. 6

F: Fresh
S: Saturated Salt

POWER

F:F ½S:F S:F ½S:S S:S
SALINITY GRADIENT

Fig. 7

POWER

0 20 40
TEMPERATURE (°C)
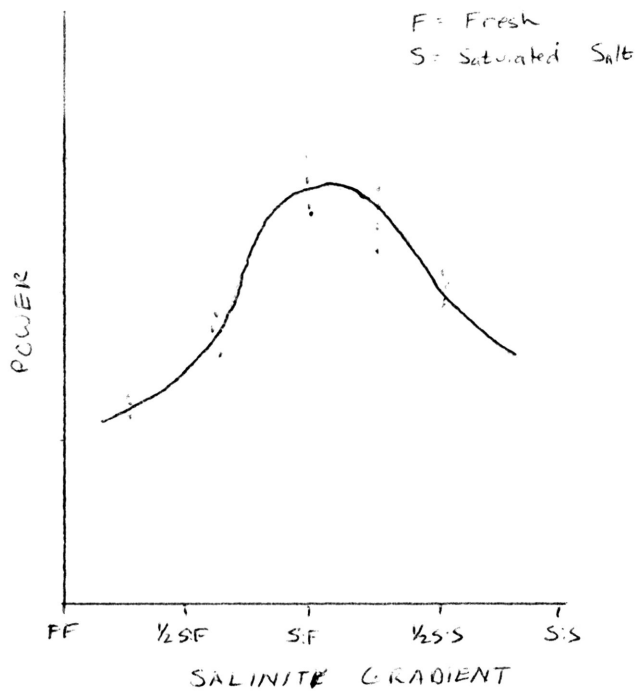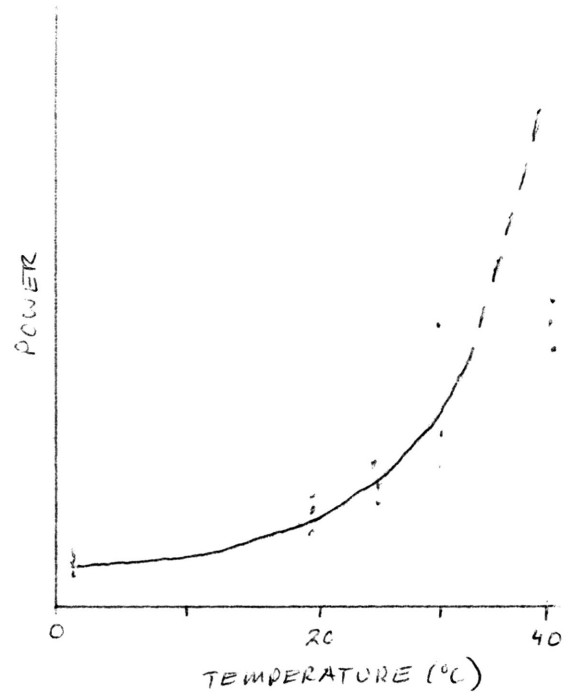
Fig. 8

ideal solutions, shown with the dashed line. The vapor pressure of salt water is depressed non-linearly, as the graph indicates. One explanation of this phenomenon is that the interaction of salt ions and water molecules, a non-ideal solvent, inhibits the vaporization of water; this interaction increases with increased salt concentration.

This helps explain the power vs. salinity graph (Fig. 7). As indicated, power outputs were greater for the same salinity gradient when that gradient was constructed with two salt solutions, rather than a salt solution and fresh water. As can be shown with Figure 5, the difference in vapor pressures is greater in the former case than in the latter. Thus there is a correlation between power output and vapor pressure difference, based on salinity gradients.

There is also a correlation for vapor pressure differences based on temperature, as is readily apparent from a comparison of Figures 6 and 8; termperature vs. vapor pressure difference and power output, respectively. Allowing for the error mentioned above, these two curves follow similar trends, and both conform to the theoretical predictions in Figure 4.

Given the above correlations, the power output of a heterosaline pump is a function of the salinity gradient and ambient temperature. In other words, the mass transfer rate is dependent on the vapor pressure difference.

Because the vapor pressure difference is the driving force of the pump, it follows that, as shown above, it is also the key to the efficiency question. An analogy can be drawn from the Carnot cycle for heat engines, for which the efficiency is the net amount of heat transferred in proportion to the total heat available for transfer. For a vapor pump, the analogs are the net amount of vapor transferred, in proportion to the total

vapor available, or:

$$E = \frac{p_O - p'}{p_O}$$

where (p_O) is the vapor pressure of the fresh or hypotonic solution, and (p') is the depressed vapor pressure of the salt, or hypertonic solution. Efficiencies based on the experimental data are shown in Tables 2 and 3:

Table 2: Efficiency vs. Salinity Gradient

Gradient	p' (mm-Hg)	p_O (mm-Hg)	E (%)
F:¼S	22.722	23.756	4.35
F:½S	21.688	23.756	8.70
F:S	19.492	23.756	17.95
⅓S:S	19.492	22.335	12.73
½S:S	19.362	21.688	10.72

Table 3: Efficiency vs. Temperature

Temperature (°C)	p' (mm-Hg)	p_O (mm-Hg)	E (%)
2	3.864	4.579	16.90
20	14.531	17.535	17.13
25	19.492	23.756	17.95
30	26.558	31.824	16.55
40	50.801	55.324	8.17

As indicated by the tables, efficiency is essentially independent of temperature, remaining at approximately 17%. Changes in salinity gradient do, however, affect the efficiency, increasing it with increased gradients. Again, the pump is more efficient if a given gradient is produced with two salt solutions, rather than a salt-fresh combination. This increase is due to the greater vapor pressure difference (p_O-p'; the numerator of the efficiency expression), as well as the decreased maximum vapor pressure (p_O; the denomenator of the efficiency expression), for a system of two salt solutions as compared to a salt-fresh system.

CONCLUSION

In conclusion, the maximum power output of the heterosaline vapor pump increases with increases in salinity gradient and ambient temperature. The efficiency of conversion of the enthalpy of mixing is limited by, and is based on the difference of vapor pressures of the system's solutions in proportion to the maximum vapor pressure ($\frac{p_0 - p'}{p_0}$). Efficiency is dependent on the salinity gradient, but independent of ambient temperature. For any given salinity gradient, both power output and efficiency can be increased by using two salt solutions, rather than a salt-fresh combination to construct a given salinity gradient.

The efficiency data generated can be used to compare different models of vapor pumps, tested under the same conditions. By comparing actual power outputs with expected maxima, the best design could be selected.

More experiments are recommended, to be conducted with varied salinity gradients at different temperatures, to better define the salinity gradient/ temperature/vapor pressure surface. Once this is done, maximum efficiencies could be calculated for a wider range of the variables, allowing more extensive research and more significant comparisons of different vapor pump models.

REFERENCES

Daniels, F. Outlines of Physical Chemistry, 8th ed. John Wiley & Sons,
        Inc.; New York (1953).

Isaacs, J. D. & W. R. Schmitt. "Ocean Energy: Forms and Prospects."
        Science, 207: 265-273 (1980).

Lee, K. L. "Membranes for Salinity Gradent Energy Production." Abstracts
        of Papers of the American Chemical Society, 180: 5 (1980).

Loeb, S. "Osmotic Power Plants." Science, 189: 654 (1975).

Norman, R. S. "Water Salination: A Source of Energy." Science, 186: 350
        (1974).

Olsson, M., et al. "Salinity Gradient Power: Utilizing Vapor Pressure
        Differences." Science, 206: 452 (1979).

Schmitt, W. R. & G. L. Wick. "Prospects of Renewable Energy from the Sea."
        Marine Technology Society Journal, 11:16-21 (1978).

Weast, R. C., ed. CRC Handbook of Chemistry and Physics, 60th ed. CRC
        Press, Inc.; Boca Raton, Fl. (1979).

Wick, G. L. & J. D. Isaacs. "Utilization of the Energy from Salinity
        Gradients." Universtiy of California, Institute of Marine
        Resources Ref. 76-9 (1976).

_____. "Salt Domes: Is There More Energy Available from Their Salt
        than from Their Oil?" Science, 199: 1436 (1978).

_____. Response to W. C. Williams (1979).

Wick, G. S. "Is Neptune's Ole Salt a Tiger in the Tank?" Oceanus,
        22(4): 28-37 (1979).

Williams, W. C. "Mineral Salt: A Source of Costly Energy?" Science,
        203: 377 (1979).

Materials

The initial vapor pressure and power experiments were run in the apparatus figured below:
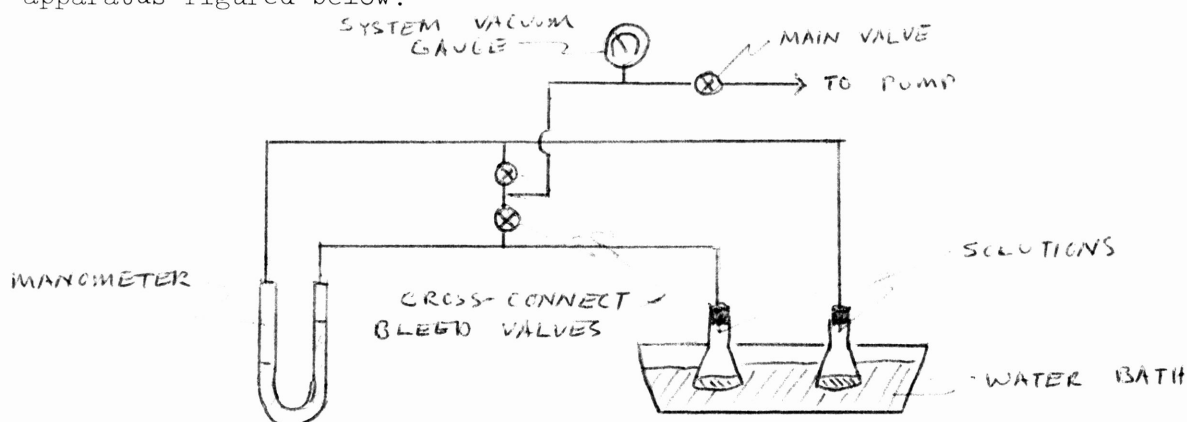
The manometer was filled with mineral oil (ρ =0.8783 g/ml), pre-treated to remove dissolved gases. Both sides of the system were of equal length and volume. The cross-connect valve allowed equilibration of the system. Solutions were held in two Erlenmeyer flasks; glass beads were added to ease boiling. The water bath was used only in temperature experiments.

Methods

The following conditions were tested:

Salinity Gradients	Temperature ($^{\circ}$C)
F:F*(control)	2
$\frac{1}{4}$S:F	20
$\frac{1}{2}$S:F	25
S:F	30
S:$\frac{1}{3}$S	40
S:$\frac{1}{2}$S	
S:S (control)	

---

*F = fresh water; S = saturated salt solution; $\frac{1}{2}$S = half the concentration of S; etc.

In the salinity experiments, ambient temperature was 24-25°C. The temperature experiments were run with saturated salt solution and distilled water; temperatures were elevated with an electric hot-plate, and depressed with ice. Actual laboratory temperatures varied by $\pm$ 0.5°C.

The general procedure was as follows:

An initial vacuum was drawn and maintained for 15 sec., after which all the valves were shut. At the end of 5 min., the difference in oil levels was noted, and the cross-connect valves were opened.

After 30 sec. of equilibration, the valves were shut again, and several readings were taken over a period of about 10 min. to establish a rate of presure change. The cross-connect valves were then opened again, and, after equilibration, another rate was measured. Three rates were taken for each run.

Each run was repeated with the flasks switched to opposite sides of the system.