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DOE/ET/20471-T2

FEASIBILITY OF USING SATURATED SOLAR PONDS FOR BRINE UNMIXING
Final Report

September 30, 1980

Work Performed Under Contract No. AC05-78ET20471

Dist-237
PT15-22

InterTechnology/Solar Corporation
Warrenton, Virginia

U.S. Department of Energy

Solar Energy

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FEASIBILITY OF USING SATURATED SOLAR PONDS
FOR BRINE UNMIXING

Final Report

30 September 1980

Prepared for the
Ocean Systems Branch
of the
United States Department of Energy
under
Contract No. DE-AC05-78ET20471

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Report No. 300980-160281

Approved by Program Manager 6 February 1981

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ABSTRACT

The overall objective of this study was to investigate in the laboratory the feasibility of using saturated solar ponds for unmixing a brine of intermediate concentration into dilute and concentrated brine streams. This objective was accomplished by conducting experiments on laboratory saturated ponds using borax, potassium perchlorate, potassium nitrate, disodium phosphate and potassium alum. Results from ponds using borax, potassium nitrate and disodium phosphate conclusively demonstrated that saturated solar ponds can self-generate and self-maintain a stable density gradient. Moreover, these ponds reestablished stable density profiles after the ponds were externally mixed.

Based on preliminary results, the residence time for unmixing of a brine of intermediate concentration into dilute and concentrated brine streams varies from a few days for the borax pond to about two weeks for the disodium phosphate pond, depending upon the characteristics of the individual saturated solution. Because of only a very small increase in the density of saturated solutions from 25°C to 90°C, the potassium perchlorate pond could not establish a stable density stratification.

The results with a three-foot-deep alum saturated pond operating between 25°C at the surface and 55°C at the bottom indicated that the residence time between these two temperature limits should be more than two weeks. Between these two temperatures, the saturation density increases from 1.06 at 25°C to 1.16 at 55°C. However, at 80°C, the saturation density is 1.45. Thus, it is possible that the residence time for the alum saturated pond between 25°C and 80°C may be less than two weeks. One more unmixing test between these two temperatures would be very desirable.

TABLE OF CONTENTS

	<u>PAGE</u>
Abstract	iii
I. INTRODUCTION	1
A. Salinity Gradient Energy Conversion and Brine Unmixing	1
B. Project Objectives	2
C. Solutes for a Saturated Solar Pond	3
D. Working Principle of a Saturated Solar Pond for Brine Unmixing	4
E. Summary	7
II. EXPERIMENTAL WORK	11
A. Experimental Set-Ups	11
B. Experimental Results	13
1. Borax Pond Tests	13
2. Potassium Perchlorate Pond Test	16
3. Potassium Nitrate Pond Tests	16
4. Disodium Phosphate Pond Tests	25
5. Potassium Alum Pond Tests	29
6. Evaluation of Other Solutes	35
III. CONCLUSIONS AND RECOMMENDATIONS	37
IV. REFERENCES	39

FIGURES

I. INTRODUCTION

A. SALINITY GRADIENT ENERGY CONVERSION AND BRINE UNMIXING

Salinity gradient energy conversion is presently being considered as a possible means for economic power generation. Specifically, "fresh" water or dilute brine, and concentrated brine are mixed under conditions such that an appreciable fraction of the free energy of mixing is converted to useful power. The effluent from such a system is a large amount of mixed brine of intermediate concentration which must be either discarded after use--an open-cycle system--or recycled back into the system--a closed-cycle system. Because of resource requirements, an open-cycle system is restricted geographically to sites possessing large supplies of fresh water or dilute brine, and concentrated brine or solid salt. In order to make such a system site-independent, it is necessary to generate dilute and concentrated brine from the mixed brine for recycling into the system.

A number of brine unmixing processes have been proposed in the literature, including solar stills and solute precipitation. Because the latent heat of vaporization of water is very large as compared to the free energy of mixing, the solar still costs become prohibitively large due to excessive area requirements. While solute precipitation may be a more energy efficient process, it involves handling and transportation of salt slurries and salt precipitation subsystems. The precipitate could also coat heat exchanger surfaces or plug pipes.

One possible way to close a salinity gradient energy conversion system is to unmix the mixed brine by means of a salt-stratified saturated solar pond system. In such a pond, the density, temperature and solute concentration increase from the top to the bottom of the pond. In order for the pond to be saturated at all levels, a solute whose solubility in water increases with temperature is employed. The potential advantage of using a saturated solar pond for brine unmixing is immediately clear. The energy input to the saturated pond is not used to evaporate water

but to supply some sensible heat and the free energy of mixing. Heat input should be less by an order of magnitude than if water is evaporated. However, the amount and therefore the cost of salt for such a pond is generally much higher than that for a conventional nonconvecting sodium chloride solar pond. Unfortunately, a conventional sodium chloride solar pond cannot be used for brine unmixing because the solubility of sodium chloride in water is almost constant with temperature.

Incidentally, it should be pointed out that while the work reported in this document was specifically aimed at developing saturated solar ponds for brine unmixing for salinity gradient energy conversion systems, it nevertheless is generally applicable to any chemical process where it is required to separate a saturated solution of intermediate concentration into a dilute and a concentrated solution.

B. PROJECT OBJECTIVES

In August 1978, Contract No. DE-AC05-78ET20471 was entered into between the United States Department of Energy and InterTechnology/Solar Corporation to develop a reverse electrodialysis salinity power heat engine in which a saturated solar pond is used for brine unmixing. The first final report on this contract summarized the status of ion exchange membranes for reverse electrodialysis and was submitted to DOE in February 1980 (1). The objective of this second final report under this contract is to present the experimental work on the technical feasibility of using a saturated solar pond system for unmixing of a mixed brine of intermediate concentration into a dilute brine and a concentrated brine stream.

Under this program, a number of potential solutes were identified which could be used both in a saturated solar pond and a salinity gradient energy conversion system. These included borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), potassium nitrate (KNO_3), disodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$), potassium alum ($\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$) and potassium perchlorate (KClO_4). Laboratory saturated pond experiments using these solutes were conducted to

demonstrate that a saturated solar pond can be used for brine unmixing. The residence time for brine unmixing was estimated based upon the laboratory experiments, the results of which are presented in this report.

C SOLUTES FOR A SATURATED SOLAR POND

An appropriate salt for the saturated solar pond must have five qualities. Three of these qualities, which refer to the physical properties of its saturated solutions over the desired temperature range, are:

- 1) The density of the saturated solution must increase adequately with an increase in temperature. This is accomplished by salts for which the solubility increases adequately with temperature.
- 2) The average solubility must not be too high.
- 3) The salt must be chemically stable, nontoxic, and transparent in solution.

The other two qualities desired of the salt refer to its cost and availability:

- 4) The salt should be very inexpensive preferably about the same price as sodium chloride.
- 5) It can be shown that for appreciable power production, a very large quantity of salt will be needed. Thus the salt must be available in very large quantities.

The potential solutes which were identified for investigation during this program are listed in Table 1. This table gives 1) the solubility of anhydrous solute in water at 30°C and 90°C; 2) the average concentration $(C_c + C_d)/2$, for a saturated pond with the top and bottom temperatures of 30°C and 90°C; and 3) the concentration difference $(C_c - C_d)$.

A saturated solar pond will be more stable if the percentage density difference (which is proportional to the percentage concentration difference) is as large as possible. Thus, on this basis potassium nitrate, potassium alum and disodium phosphate would be most attractive.

It should also be noted from this table that the average solubility of many of these solutes is significantly larger than 0.15 gm. of solute per gm. of water, which is approximately the average solubility of NaCl in an ordinary solar pond using NaCl. Thus, for the solutes given in Table 1, a saturated solar pond will require a greater quantity of salt which is significantly more expensive than NaCl as compared to the conventional NaCl solar pond. But it should be realized that a NaCl pond cannot be used for brine unmixing because the solubility of NaCl in water is fairly constant at about 26%.

For brine unmixing applications it is necessary to use a saturated solar pond. The working principle of such a system is explained in the next section.

D. WORKING PRINCIPLE OF A SATURATED SOLAR POND FOR BRINE UNMIXING

A saturated solar pond is a salt-stratified solar pond in which each layer of salt solution is saturated with salt at the temperature of the layer. In such a pond there will be no salt diffusion from the bottom to the top layer because the pond is fully saturated at each level.

To accomplish separation of the mixed brine into dilute and concentrated brine streams, the mixed brine enters the pond from one side at a level in the middle of the pond where the temperature and the density of the mixed brine are equal to the temperature and density of the pond solution at that level. The dilute and concentrated brine streams are withdrawn from the top and the bottom of the pond, respectively, from the opposite side of the pond.

TABLE 1
SOLUBILITY DATA OF POTENTIAL SOLUTES FOR A SATURATED SOLAR POND

Solute	Chemical Formula	Solubility gm/gm Water		$C_c - C_d$	$(C_c + C_d)/2$	Percentage Concentration Difference	Reference Code
		30°C C_d	90°C C_c			$C_c - C_d$ $(C_c + C_d)/2$	
Sodium tetraborate (borax)	$Na_2B_4O_7$	0.039	0.41	0.371	0.225	1.65	Perry
Potassium perchlorate	$KClO_4$	0.026	0.18	0.154	0.103	1.50	Perry
Potassium aluminum sulfate (alum)	$K_2Al_2(SO_4)_4$	0.084	1.09	1.006	0.587	1.71	Perry
Sodium bisulfate	$NaHSO_4$	0.32	0.90	0.580	0.610	0.95	Lange
Potassium nitrate	KNO_3	0.458	2.02	1.562	1.239	1.26	Perry
Disodium phosphate	Na_2HPO_4	0.208	1.03	0.822	0.619	1.33	Perry

¹ Chemical Engineers' Handbook, Ed. Robert H. Perry et al, Fourth Edition, 1969,
McGraw-Hill Book Company, New York.

² Lange' Handbook of Chemistry, Ed. John A. Dean, Twelfth Edition, 1979,
McGraw-Hill Book Company, New York.

To maintain the mass balance, the mixed brine feed divides into two streams. The stream equal to the flow of dilute brine moves up, while that equal to the flow of concentrated brine moves toward the bottom layers in the pond. The fraction of the mixed brine feed which moves up loses heat to the upper layers and cools down, thereby releasing salt which, being heavier than the surrounding solution, slowly falls to the bottom layers. The part of the mixed brine which moves down is cooler and less dense than the bottom layers. The energy which must be supplied to the pond is comprised of 1) the sensible heat to heat the fraction of the mixed brine feed moving to the bottom layers to the bottom temperature and 2) the free energy of unmixing of the mixed brine into dilute and concentrated brine streams, which is generally a very small fraction of the sensible heat.

The flow rates of the different streams are so adjusted that the time taken by a parcel of mixed brine entering from the side of the pond (in moving to the exit ports located at the top and the bottom of the opposite side of the pond) is greater than either:

- 1) The time taken by solar energy to heat the fraction of the mixed feed moving down to the temperature of the bottom layers. This depends upon solar insolation, pond depth, and the geometry of the pond;
- 2) The chemical unmixing time for the particular salt. This is the time taken by the salt to dissolve or to precipitate from a saturated solution when its temperature is slowly increased or decreased--as for the mixed brine stream fractions going to the bottom layers and top layers, respectively. This depends solely upon the chemical characteristics of the salt-water solution.

In other words, the residence time should be greater than the chemical unmixing time as well as the time taken by the sun or any other energy source to heat the mixed brine to the temperature of the bottom layers.

Further details on the modeling of saturated solar ponds for brine unmixing are given in Reference 2.

One of the objectives of the experimental work was to estimate the minimum residence time required for a saturated solar pond to unmix a mixed brine into dilute and concentrated brine streams.

E. SUMMARY

The objectives of this study were 1) to investigate the feasibility of using saturated solar ponds for unmixing a brine of intermediate salinity into dilute and concentrated brine streams, and 2) to determine the minimum residence time necessary to accomplish this unmixing by the pond. These objectives were accomplished by conducting experiments on laboratory saturated ponds using a number of different solutes.

A one-foot deep plastic circular tank was used to conduct the saturated pond experiments with borax, potassium perchlorate and potassium nitrate. For the disodium phosphate saturated pond a rectangular polypropylene tank (2' x 4' x 3' deep) was used, while the potassium alum saturated pond experiments were conducted in a rectangular polypropylene tank (2' x 4' x 3' deep) with a metal plate. The first two ponds were heated by means of copper heat exchangers at the bottom of the pond with a constant temperature hot water bath; the third pond was heated by means of electrical heating tapes under the metal bottom. The temperature profiles in the ponds were measured by means of a string of copper-constantan thermocouples which were placed at different depths in the center of the pond. The density profiles were measured by suspending a plummet, attached to a polyester thread, to the desired depth and noting the density by using a Troemner balance.

It was found that to start a pond, it could be stratified either by filling it in three to ten layers or by starting the heat after the salt and water had been added to the tank. The latter technique was found to be more time consuming because the salt had to slowly diffuse from

the bottom to the top of the pond. In both of these techniques, the pond must be heated gradually to make sure the pond does not get uniformly mixed due to spontaneous thermal convection at the bottom of the pond.

The borax saturated pond tests showed that it can self-create and maintain a stable temperature gradient of about 0.6°C per cm. with a surface temperature of 38°C and a bottom temperature of about 60°C . To estimate the unmixing time, on 2 February 1979, when the pond had a ΔT of 25°C , it was purposely mixed up by means of a stirrer. Within eighteen hours of the mixing the pond developed a ΔT of 19°C on its own. While the pond very quickly attained the same temperature at the bottom as it was before mixing, the surface temperature was still higher by approximately 6°C eighteen hours after the mixing was stopped. Based on this preliminary test, it appears that the residence time for brine unmixing in a borax saturated pond should be on the order of only a few days.

Because of a very small increase in the saturation density of the potassium perchlorate solution-- 1.015 gm/cc at 30°C to 1.069 gm/cc at 90°C --a stable saturated pond could not be established in the laboratory. This indicates that an increase in saturation density with temperature is necessary but not a sufficient condition for pond stability. For an actual pond to be stable, the density increase should be greater than a minimum threshold value which depends upon the operating conditions: wind velocity, fluid velocities for withdrawal and injection of brine into the pond, etc. It appears that the density increase from 1.015 to 1.069 for KClO_4 was lower than the threshold value.

Experiments with the saturated potassium nitrate pond were started by filling the pond in ten different layers. It was found that the pond can sustain a temperature gradient of 1.4°C per cm. with a surface temperature of 25°C and a bottom temperature of 68°C . The pond was then deliberately mixed up, but no unmixing tendency was observed because of an insufficient quantity of salt in the pond. After the pond was allowed to cool to room temperature, it was gradually heated by

increasing the heater temperature in small steps for two weeks. The pond finally established a stable ΔT of about 15°C with the pond bottom temperature of about 40°C . This demonstrated that a saturated potassium nitrate pond can self-generate a stable temperature gradient of 0.4°C per cm. These tests also proved that the pond takes much longer to self-generate a stable stratification as compared to filling the pond in different layers.

Tests were also conducted on a KNO_3 saturated pond with intermittent heating. Results of 13 cycles of four-hour heating and four hours of no heating demonstrated that the pond is capable of recovering its original temperature profile without any noticeable change. After 13 cycles of a six-hour cycling test, the pond temperature profile was slightly modified. There was a further deterioration of pond temperature profile after the eight cycles of an eight-hour cycling test. These tests caused the pond surface to rise and the bottom temperature to fall. This was primarily due to very high heating rates at the beginning of the heating periods as explained in the report.

A salt precipitation test was run on a KNO_3 saturated pond. During this test no salt precipitation was observed for three days while the pond temperature was 3°C below the saturation temperature. It was found that the solute started precipitating when the pond temperature was about 8°C below the saturation temperature.

The disodium phosphate pond was started by filling it in two layers. The pond reached a steady state after about three days with the top and bottom temperatures of about 20°C and 55°C respectively. Two unmixing tests were conducted on this pond. The first test conclusively demonstrated that if the pond is fully saturated at each level, the pond residence time for brine unmixing should be about two weeks. The second unmixing test demonstrated that if the pond is not fully saturated, a complete unmixing may not be achieved even if the pond has a stable density stratification.

We experienced some difficulty in establishing a saturated alum pond by itself. It was found that an alum solution can be cooled by as much as 20°C below its saturation temperature without any significant solute precipitation. Due to this a stable alum pond stratification could not be generated from a mixed pond. However, it was fairly easy to stratify the pond by filling it in layers and then suspending salt bags to make it fully saturated at all levels. A pond unmixing test was conducted with the top and bottom temperatures of 25°C and 55°C, respectively. For this temperature range it was found that the pond residence time should be more than two weeks for brine unmixing. However, it is possible to have a residence time of two weeks or less if the pond's bottom temperature is about 80°C. The saturation density increase from 25°C to 80°C is 1.06 to 1.45 as compared to 1.06 to 1.16 only for the saturation temperatures of 25°C to 55°C. It is recommended that one more alum pond unmixing test with the top and the bottom temperatures of approximately 25°C and 80°C should be undertaken.

II. EXPERIMENTAL WORK

The laboratory work to investigate the feasibility of brine unmixing by a saturated solar pond was carried out using borax, potassium perchlorate, potassium nitrate, disodium phosphate and potassium alum. While borax, potassium perchlorate and potassium nitrate are attractive solutes for reverse electrodialysis, potassium alum and disodium phosphate are good candidates for osmotic pressure salinity gradient systems. Data on solubility and saturation density of all these solutes in water as functions of temperature were generated in the laboratory and are presented.

A. EXPERIMENTAL SET-UPS

A circular plastic pond 283 mm in diameter and 340 mm in depth was used for the borax, potassium perchlorate and potassium nitrate tests. The pond was heated by means of a 6.35 mm OD type L copper heat exchanger coil at the bottom of the pond. The details of this pond are shown in Figure 1. The objective of the borax tests was to learn, in general, about the behavior of saturated ponds--particularly about how to stratify such a pond, how to measure the temperature profiles, how to maintain a constant pond depth and to determine if such a pond can regenerate itself after complete mixing. The potassium nitrate pond was used to investigate the behavior of saturated ponds under cyclic heating and no heating. A salt precipitation test was also performed on the KNO_3 pond by letting the pond slowly cool below its average saturation temperature.

A rectangular polypropylene tank (2' x 2' x 3' deep) with a plastic bottom was used for the disodium phosphate tests. A schematic diagram of this pond is shown in Figure 2. In this pond also a coiled heat exchanger made from 6.35-mm OD type L copper was used to heat the pond at the bottom. Two brine unmixing tests were conducted with this pond and are discussed later in this section. In both this tank and the

circular tank, an external bath and a pump were used for circulating hot water through the heat exchanger.

A rectangular polypropylene tank with a metal bottom was used for alum tests. The tank was made by welding two polypropylene pond shells (each 2' x 2' x 3' deep) together. To allow for a metal bottom, a 3" polypropylene flange was welded to the shell. The shell was bolted to a stainless steel metal plate (Carpenter 20-cb-3) which acted as the bottom of the pond. The pond was heated from below the metal plate by means of electrical heating tapes of 96-watt capacity each at 110 volts. However, the heat output from these tapes could be controlled by varying the voltage through a variac. An unmixing test for 22 days was run on this pond, and this test is discussed later in this section. This pond is shown in Figure 3.

Temperature measurements in the ponds were made by means of copper-constantan thermocouples hooked to a Digitrend digital temperature logging scanner. The Digitrend could scan temperature profiles automatically after a fixed time interval. A string of thermocouples was fixed on a stainless steel rod which was placed in the center of each pond. Thermocouples were also used for measuring the ambient air temperature, inlet and outlet water temperatures to and from the heat exchangers used for pond heating, and the temperature of various flow streams entering and leaving the pond during the unmixing tests.

To maintain a constant pond depth, a water bird bath was used at the top of the pond to provide a continuous supply of water to compensate for any evaporation from the pond surface. A bird bath is a very simple but accurate arrangement which works on the gravity feed principle to maintain a constant liquid level. This device was developed at Inter-Technology/Solar Corporation during the course of this contract. Its working principle can be understood by referring to Figure 3.

The densities in the pond were measured in situ very accurately by means of a Troemner balance, which works on Archimedes' principle. In this

set-up an epoxy-encapsulated plummet is lowered by means of a 0.13-mm diameter polyester thread to the point where the density is required. The weight loss of the plummet due to buoyancy of the surrounding solution is directly related to the density of the surrounding solution. This balance is capable of reading densities up to ± 0.0001 .

For the unmixing tests with the disodium phosphate and potassium alum ponds, the dilute and the concentrated brine streams were withdrawn from the top and the bottom of the pond, respectively, by means of two adjustable-rate peristaltic pumps. These streams were mixed in a closed glass flask by means of a magnetic stirrer and heated before returning to the middle of the pond. The level where the mixed brine entered the pond was determined on the basis that the pond density and temperature at that level were equal to those for the mixed brine streams.

Heating the mixed brine was done to make sure that the temperature of the mixed brine at the point where it entered the pond was equal to the temperature of the pond at that location. Thus, no convection current was generated because of a difference between the temperature of the mixed brine and the pond temperature at the point where this stream entered the pond. No pump was used on the return line because the pressure build-up from pumping the dilute and concentrated brines to the flask was sufficient to pump the mixed brine back into the pond. Tygon tubing (of 1/16" ID and 1/8" OD) was used for circulating all the streams. The concentrated brine stream was always maintained above the precipitation temperature by at least 5°C by heating this stream at the pond outlet by means of an electrical heating tape wound around the exit line. Figure 4 shows the mixing arrangement.

B. EXPERIMENTAL RESULTS

1. Borax Pond Tests

The saturation density and solubility of borax in water as functions of temperature were generated in the laboratory and are shown in Figure 5.

As described before, a circular plastic tank 283 mm in diameter and 340 mm deep was used for the borax saturated pond. The pond was heated by means of a heating coil at the bottom of the pond. The main purpose of this pond was to learn about the characteristics of a laboratory saturated pond. Several short-term tests were conducted, and it became clear very quickly that to increase the pond temperature, the heat input rate should be increased very slowly--in steps of only about 1 to 3°C--depending upon the actual temperature, the saturation temperature and the quantity of excess salt available at the bottom of the pond.

a. Self-Generation Tests

Two tests were conducted to demonstrate that stable density and temperature profiles in the borax pond can be generated by gradually heating the pond. In the first test, the pond was heated to a uniform temperature of about 67°C to get all the solute into the solution. Then it was allowed to cool down slowly. Once the pond surface temperature reached about 36°C, the pond was slowly heated by increasing the temperature of the water bath in small steps. In this way the pond developed a temperature differential ΔT (between the bottom layer and the surface layer) of about 45°C over a period of 5 days. During this period the surface temperature was constant around 36°C. At this stage the pond heater temperature was held fixed around 82°C. During the following five days the pond surface temperature gradually increased, which resulted in a decrease of ΔT to about 25°C, and it had approximately reached a steady state. This was the first test demonstrating that a saturated pond can generate a stable density profile on its own. Unfortunately, this test could not be continued due to heater failure.

For the second test, the pond from the first test was allowed to cool by turning off the heat completely. The pond became essentially uniform in temperature at about 35°C and was not convecting. There was a considerable excess of salt ($\text{Na}_2\text{B}_4\text{O}_7$ and hydrates) in the pond. Circulation of water from the bath was begun in the heating coil at a bath temperature of 40°C. During the next two days, the bath temperature was increased by 3

to 5°C periodically until a bath temperature of 60-65°C was attained. This temperature (lower than that in the first test) was held constant for the next 18 days until the end of this test. On 3 February the temperature differential ΔT between the bottom of the pond and the top surface was 28°C. This temperature differential progressively decreased to 19°C on 12 February, as shown in Figure 6, due to a continual increase in the surface temperature. This temperature difference was maintained for six days, i.e., until 17 February at 1815 hours, and was not affected by deliberately stirring the pond on 14 February in a region between 2-1/2 and 5 cm from the bottom of the pond.

On 9 February the density of the brine was measured at the top and the bottom of the pond, and at a level 10 centimeters above the bottom. These densities compared well with the saturation density at the temperature of each level. It was concluded that the pond was saturated at each level.

b. Unmixing Test

In order to investigate whether a saturated borax pond can regenerate a stable density profile, a short pond unmixing test was conducted. On the afternoon of 21 February, the pond had a temperature differential of 25°C. At 1500 hours the pond heating was stopped and the pond was mixed to an essentially uniform temperature of about 54°C. The heating was resumed one-half hour later at a bath temperature of 65°C. The purpose of this test was to examine once more the capability of the pond to reestablish a stable temperature gradient. According to the data on 21 and 22 February, the gradient was fairly well reestablished within less than one day of the stirring. A temperature difference between top and bottom layers of 19°C was observed in less than 18 hours after the mixing was stopped, as shown in Figure 7.

c. Discussion

The three tests described above clearly demonstrated that a one-foot deep borax saturated pond can self-create and sustain a temperature

differential of about 19°C without any external maintenance of salt gradient or initial salt concentration stratification. However, a significant quantity of excess solute was present at the bottom of the pond during the second and third tests. Secondly, based on the results of these preliminary tests, it appears that the residence time for the mixed brine coming from a salinity gradient energy conversion system should be of the order of a few days before it can be separated into dilute brine at the top and concentrated brine at the bottom of the pond.

2. Potassium Perchlorate Pond Test

The solubility of KClO_4 according to published literature increases from 2.2 gm/100 gm of water at 25°C to about 16 gm/100 gm of water at 85°C. The density and concentration of KClO_4 saturated solutions were measured as functions of temperature and are given in Figure 8. The density data indicate that up to about 60°C there is no appreciable increase in the density of KClO_4 saturated solution.

An unsuccessful attempt was made to establish the KClO_4 stratified saturated pond using the one-foot-deep plastic circular tank. However, after trying for about two weeks, it was decided to stop working with this solute. Apparently the relatively small change in density per degree for KClO_4 solutions (see Figure 8) was insufficient to give stable, i.e. nonconvecting, conditions in the pond. Secondly, right from the beginning of this test, it was observed that the galvanized iron fitting at the bottom of the tank was attacked by KClO_4 . It was evident by the appearance of a very dark rust coloration of the fitting due to corrosion.

3. Potassium Nitrate Pond Tests

The one-foot circular plastic pond which was used for borax was also used for the potassium nitrate pond. Tests were conducted to demonstrate that a potassium nitrate pond can generate a stable density

profile and if mixed can recreate this profile. To simulate periods of no solar energy and to get an idea of the pond unmixing time, 4-hour, 6-hour, and 8-hour heating and no heating cycle tests were conducted. A salt precipitation test was also conducted to estimate the degree of cooling below saturation temperature required for KNO_3 to precipitate from the solution. These tests are discussed in detail in the following subsections.

a. Initial Stratification and Regeneration

The pond was filled with 10 layers of potassium nitrate solution, varying in concentration from 0 to 55.5 weight percent potassium nitrate and having an average pond concentration of 33.8% and average density of 1.26 gm/cc. The temperatures of solutions made for different layers varied from 20° to 65°C. Figure 9 shows the solubilities and densities of potassium nitrate saturated solutions as functions of temperature. The temperature of the heating coil at the bottom of the pond was set at 70°C while the pond was being filled. This setting caused the temperature of the pond bottom to rise from 65°C to 67.5°C with a temperature difference of 43°C between the top and bottom layers of the pond within 24 hours after the pond was filled. This temperature difference between the top and bottom layers, ΔT , stayed between 40°C and 44°C over a period of 12 days. A slight variation in ΔT was observed because of variations in the ambient temperature.

Figure 10 shows the temperature profile in the pond during an 11-day period. During the first five days a decrease in the temperature gradient at the bottom of the pond was observed, as can be seen from Figure 10. After the first five days the pond was stabilized and continued to be stable for the next 6 days. The temperature difference between the top and bottom layers of the pond was around 43°C on the average. Therefore, it was concluded that a stable potassium nitrate pond can be obtained by layering it to fill it, and an appreciable temperature gradient (about 1.3°C/cm) between the top and bottom layers can be maintained.

After 12 days the pond was deliberately mixed to see if it could unmix on its own under the original conditions of heating. No unmixing tendency was observed during the first 24 hours, primarily because there was insufficient salt in the pond for saturation. As can be seen from Figure 9, for an average concentration of 33.8% the saturation temperature is about 33°C, while the pond temperature after mixing was 50°C. The pond was then allowed to cool down by turning off the heater for the next 24-hour period. At the end of this cooling period the pond was at a uniform temperature of 29°C. The heating bath was then turned on with a temperature of 33°C. This temperature was gradually increased to 43°C over the next 8-hour period. A tendency to unmix and self-generate the stratification was observed. The heating bath temperature was then increased to 46°C. This time, convection currents were visually observed, and the pond did not achieve regeneration in 3 days. Again, this was because of a high heating rate and insufficient salt in the pond.

The pond was then reprecipitated by turning off the heat for one day. The following day the pond was observed to have a uniform temperature of 23.6°C with some potassium nitrate crystals at the bottom. The heater was again turned on the next day but at a much lower temperature setting of 30°C. This temperature was gradually increased to 36°C over a period of 24 hours. This time, the pond was observed to be regenerating. After 8 days the heating rate was slightly increased by increasing the heater temperature from 36° to 38.5°C. During the following 4 days the pond was found to be stabilizing, and so the heater temperature was increased to 41°C. The heater was then left at 41°C, and a stable pond was obtained.

During the first 3 days after the heater temperature was changed to 41°C, the ΔT between the top and bottom layers of the pond was found to be between 13.5 and 14.9°C, which was later stabilized around 15°C and stayed at this value for the next two weeks. Thus, it was concluded: (i) that a potassium nitrate saturated pond can self-generate and self-maintain stable density and temperature gradients provided there is

sufficient salt in the pond, and (ii) a ΔT of 14°C to 15°C between the top and bottom layers of a one-foot-deep potassium nitrate pond (or $0.4^{\circ}\text{C}/\text{cm}$) can be maintained. While the ΔT and the temperature gradient of $0.4^{\circ}\text{C}/\text{cm}$ are lower than their corresponding values before pond mixing of about 42°C and the $1.3^{\circ}\text{C}/\text{cm}$, these results show that a potassium nitrate pond can be stable with a much smaller density gradient or a much lower salt concentration gradient.

b. Heating and Cooling (No Heating) Tests

To study the effect of intermittent cooling on the stability of a saturated solar pond during night or periods of very low solar insolation, three separate tests of 4-hour, 6-hour and 8-hour intermittent heating and cooling were carried out. Results of these tests are discussed in the next section. The heating bath temperature was kept constant at 41°C during heating in all these intermittent heating and cooling tests.

i. Exploratory Intermittent Heating Tests. After 2 weeks of constant-temperature heating at 41°C , an intermittent heating test was started by first switching the heater off for 5 hours, thereby allowing the pond to cool down. During this five hours of cooling, temperature profiles were measured at 30-minute intervals. The temperature difference between the top and bottom layers during the cooling period dropped from 15.4°C to 8.8°C , while the bottom temperature went down from 38.8°C to 32.9°C . The pond was then reheated by first switching on the heating bath at 34°C for 2 hours, and then the bath temperature was increased to 41°C . This heating was continued for 40 hours in order to see whether the temperature profile in the pond could be regenerated by maintaining the heating coil at 41°C or not. The temperature profile measured at the end of 40 hours heating was identical to that before cooling started, indicating that the pond can be regenerated after a short period of cooling.

After 40 hours of heating, the heater was again turned off for 4 hours. During this cooling period, the bottom temperature dropped from 38.9°C

to 33.1°C. and the temperature difference between the top and bottom layers, ΔT , dropped from 15.8°C to 9.2°C. After 4 hours, the heater was switched on again. It was observed during this heating period that a temperature difference of 13.8°C between the top and bottom layers of the pond was established during the first half hour of heating and remained at this value during the next 3-1/2 hours of heating. The temperature profile measured after 4 hours of heating was somewhat different from the one before cooling. Also, the value of ΔT was lower by 2°C, so that it was decided to leave the heating on for one more day. Figure 11 shows this 4-hour cooling and heating cycle. The temperature profile measured after a 1-day heating was found to be identical to that measured before cooling, indicating that the pond had stratified to its original profile.

ii. Four-Hour-Cycling. It was then decided to study the effects of 4 hours of cooling (more correctly, no heat input) and 4 hours of heating cycles on the stability of the pond and to observe if any salt precipitated during the cooling periods. The heating was switched off for 4 hours and then switched on for 4 hours. This procedure of heat on and off after each 4-hour period was continued for 13 cooling and heating cycles. The temperature profile measured at the end of the 13th cycle was found to agree well (within the accuracy of the experimental set-up) with the temperature profile at the beginning of the first cooling cycle. The hourly data on temperature profile indicated that most of the pond recovery, after the cooling period, occurred during the first hour of heating and that the pond was fully recovered during each heating cycle. Figure 12 is a plot for the 6th cycle, which was typical of all cycles.

Figure 13 shows the maximum and the minimum temperatures observed at any point in the pond at the end of cooling and heating periods during 13 cycles. It also compares the temperature profile at the beginning of the first cooling cycle with that at the end of the 13th heating cycle. From Figure 13, it can clearly be seen that the variation in temperature at any point in the pond after 4 hours of heating or 4 hours of cooling

was less than 3°C during all 13 cycles. One reason for this variation is the slight variation in pond temperature with the change in the ambient temperature, which was consistently observed with the pond testing. After the 13th cycle on 25 June 1979, the heater was left on for 16 hours overnight.

During this 4-hour cycling test, no salt precipitation was visually observed even after 4 hours of no heat input to the pond. One other observation that can be made from Figures 12 and 13 is that, at the end of the cooling periods, the temperature at the bottom of the pond was slightly lower than that 3 cm above it. This was probably due to the fact that most of the heat loss takes place from the bottom of the pond, thereby reducing the bottom temperature.

iii. Six-Hour-Cycling. The next morning a 6-hour cooling and 6-hour heating cycle test was started by switching off the heater for 6 hours at 0900 hours on 26 June 1979. The heater was switched off and on automatically at 6-hour intervals. Temperature profiles were measured every hour during this test. The pond was also checked for any salt precipitation during the cooling cycles. At the beginning of this test, the temperature at the bottom was 39.5°C, and the temperature difference between the top and bottom layers was 17.1°C. At the end of the first cooling period, the temperature at the bottom and ΔT dropped to 32.1°C and 8°C, respectively and no salt precipitation was observed. However, at the end of the first heating cycle, the temperature at the bottom and ΔT were both somewhat lower than their starting values. It was decided to continue this test in order to see how the temperature profile is modified. Figure 14 gives the temperature profiles during the 9th cycle, which was typical for the different cycles.

Figure 15 shows the maximum and minimum temperatures observed at any point in the pond at the end of cooling and heating periods for 13 successive cycles, along with the temperature profiles at the beginning of the first cycle and at the end of the 13th heating cycle. From Figure 15, it can clearly be seen that the variation in temperature at

any point in the pond after 6 hours of heating or 6 hours of cooling was less than 3°C during all 13 cycles. At the end of the 13th heating cycle at 1500 hours on 2 July 1979, the heater was left on overnight.

In these 6-hour tests the temperature profile was slightly modified after the first cycle, and this new profile had a ΔT of about 5° to 6°C lower than at the start of the first 6-hour cooling cycle, mainly because the surface temperature went up by about 3°C. Once again, no precipitation was observed during any of the cooling cycles.

iv. Eight-Hour Cycling. The following morning on 3 July 1979, it was decided to see the effect of 8 hours of heating cycles on the stability of the pond and on salt precipitation by switching off the heater for 8 hours at 0900 hours. The heater was switched off and on at 8-hour intervals. Temperature profiles were measured every hour during this test. The pond was also checked for any precipitation during cooling cycles. At the beginning of this test, the temperature at the bottom was 38.4°C, and the temperature difference between the top and bottom layers, ΔT , was 13.2°C. At the end of the first cooling period, the temperature at the bottom and ΔT dropped to 29.3°C and 4.4°C, respectively, and no salt precipitation was observed. However, at the end of the first heating cycle, the temperature at the bottom and ΔT were 37.9°C and 12.5°C, respectively. Since the bottom temperature and ΔT both were somewhat lower than at the start of the 8-hour cycling test, it was decided to continue this test in order to see how the temperature profile was modified by 8-hour cycling. Figure 16 represents a typical plot for the 5th cycle.

Figure 17 shows the maximum and minimum temperatures observed at any point in the pond at the end of the cooling and heating periods for 8 successive cycles, along with the temperature profiles at the beginning of the 8 x 8 test, and 192 hours after the heating was started for the 8th cycle. From Figure 17, it is clear that the variation in temperature at any point in the pond after 8 hours heating or 8 hours cooling was

less than 3.5°C during all the 8 cycles. These 8-hour cycling tests indicate that the temperature profile was slightly modified due to cycling.

This new profile, as shown in Figure 18, indicated that the temperatures at any point in the bottom part of the pond were slightly lower than the corresponding temperatures at the beginning of the 8 x 8 cycle test, while the temperatures in the upper part of the pond were somewhat higher than the corresponding temperatures at the start of the cycling test. The modified temperature profile has a ΔT of about 3.4°C lower than at the start of the first 8-hour cooling cycle, mainly because the surface temperature went up by about 2°C. However, the temperature drop in most of the pond was not more than 1°C from the initial temperature due to the 8-hour cycling test. Once again, no precipitation was observed during any of the cooling periods.

After the 8th cycles the heater was left on at 41°C. During this heating it was observed that the temperature profile never came back to the one before the cycling test. As a matter of fact, after 184 hours of additional heating at 41°C after the cycling test, it was observed that the temperature at every point became higher than its corresponding value at the end of the 8 x 8 test.

v. Discussion of Results. As is evident from Figure 18, the temperature profile was the same at the beginning and at the end of the 4-hour cycling test. However, after the 6-hour and 8-hour cycling test, there were small modifications of the temperature profile which caused the surface temperature to rise and the bottom temperature to fall. This was primarily due to a very high heating rate at the beginning of the heating periods. In particular, when the heating was turned on (at the end of the cooling period), the temperature difference between the coil temperature and the pond bottom temperature was about 9°C and 12°C for the 6-hour and 8-hour cycling tests, respectively. This is a significant fraction of the initial temperature difference ΔT of about 17°C before the start of the 6-hour and 13.2°C for the 8-hour cycling test. Because

of this sudden intense heating, the pond was mixed, resulting in the decrease of ΔT from 17°C to 12°C during the 6-hour cycling test and from 13.2°C to 9.8°C during the 8-hour cycling test.

This kind of information is very useful in determining the necessary density gradient for properly designing a solar pond for very sunny periods. One other way to analyze these results for the 8-hour cycling test is that even though the pond had an initial ΔT of 13.2°C , it dropped to only 4.6°C , after the first cooling period, indicating that the pond was almost uniform in temperature. However, after the heating period, the ΔT increased to 12.5°C , indicating the capability of saturated solar ponds to recreate the stable stratification even under intense heating conditions.

c. Salt Precipitation Test

Eight days after the 8-hour cycling test, a precipitation test was started by reducing the bath temperature from 41°C to 32°C --one degree below the pond saturation temperature of 33°C . No precipitation was observed during the first 29 hours. The temperature of the bath was then further reduced to 30°C and then again to 29°C after a day, but still no precipitation was observed.

On the next day it was decided to turn off the heater. Again, no precipitation was observed after 8 hours. The heater was left on at 30°C for 72 hours but no precipitation was observed. The heater was then purposely left off overnight. The next morning at 0830 hours, precipitation was observed in the pond while the pond temperature was 24.5°C --about 8°C below the saturation temperature.

The potassium nitrate pond test was then stopped with the precipitation of the solute.

d. Summary of KNO_3 Tests

In summary, these experiments on a potassium nitrate saturated laboratory pond have conclusively shown that a saturated solar pond has the capability to self-generate a stable density profile. Furthermore, it can

maintain stable density and temperature gradients by itself. It is capable of regenerating after complete mixing. Results of 4-hour, 6-hour, and 8-hour cycling tests have shown that, after short periods of cooling, a potassium nitrate saturated solar pond is capable of recovering by itself. The steady-state density and temperature profiles were reached at the end of the first complete cycle. During the precipitation test it was observed that the salt did not precipitate even after three days when the pond was at a uniform temperature of 30°C--about 3 degrees below the saturation temperature. The salt was observed to be precipitating when the pond temperature had dropped about 8°C below its saturation temperature.

4. Disodium Phosphate Pond Tests

This pond was made of a square propylene tank (2' x 2' x 3' deep), which is shown in Figure 2. The concentration and density of the saturated disodium phosphate solution in water as a function of temperature, as determined in our laboratory, are shown in Figure 19. A coiled heat exchanger made from 50' long, 1/4" OD, type L copper tubing was installed at the bottom of the pond for heating. An external bath and a pump were used for circulating hot water through the heat exchanger.

The pond was started by filling half of it with 50°C water. The amount of disodium phosphate corresponding to the average solubility of the pond solution was calculated, weighed and placed in the pond. The solution was stirred vigorously while the remaining water was added. Average solubility was calculated by taking the average of the solubilities corresponding to the surface and bottom temperatures. The bottom temperature inside the pond was maintained close to 55°C by adjusting the temperature of the heating bath. Data on temperature and density profiles were taken from time to time to determine the stratification in the pond. The pond reached a steady state after about 3

days. It therefore appeared that disodium phosphate can make a stable saturated pond.

a. Unmixing Tests

The results of two unmixing tests performed on the disodium phosphate saturated pond are discussed here. The apparatus for the unmixing test was comprised of copper tubes placed inside the pond at 2 cm and 76.5 cm below the surface for withdrawal of dilute and concentrated brine streams, respectively, in the first test. In the second test, the location of the dilute brine withdrawal port was changed to 4 cm below the surface of the pond, and in place of copper tubing glass tubing was used for the dilute brine stream. The withdrawal of the dilute and concentrated brines was accomplished by two adjustable-rate peristaltic pumps. The dilute and concentrated brine streams were brought into a closed flask where these two streams were mixed together and heated before returning to the pond at 31 cm and 21.75 cm below the pond surface during the first and second tests, respectively. The mixed stream was heated to make sure that its temperature was equal to the pond temperature at the level where it entered the pond. Other details of the unmixing test apparatus were described before in the experimental set-up subsection.

Before starting the first unmixing test*, it was ascertained that the pond was fully saturated. This was done by measuring pond density and temperature at different levels and then confirming from Figure 19 that the salt concentration corresponding to the actual density measurement was at least equal to or larger than the salt solubility at the measured temperature at that level. At the levels where this condition was not satisfied, salt crystal rods, prepared in a separate pond, were suspended in the pond. In general, based upon Figure 19, it was found that the pond was supersaturated at all levels. It is believed that complete

*The first unmixing test was conducted under a different U.S. DOE contract (No. ET-78-C-59630). A disodium phosphate saturated laboratory pond was also used for energy extraction, as are conventional solar ponds (Reference 3).

saturation or supersaturation (depending upon the characteristics of the solute) of the pond is very necessary if it is to be used for brine unmixing.

In the first unmixing test, the dilute brine and concentrated brine flow rates were maintained at 62 cc/min and 100 cc/min, respectively. For these flow rates the net circulation time for the pond between the two withdrawal ports was 1.15 days or about 28 hours. This unmixing test was run continuously for 37.5 hours, thereby turning the pond over 1.35 times. After the test the pond was allowed to regenerate by itself while the heat was left on. Density and temperature profiles before, during, at the end of the unmixing test and 13 days after that are shown in Figures 20 and 21, respectively.

This was quite a severe test in the sense that the flow rates were so large that the entire pond was circulated in only about one day. The objective of this test was to determine that if the pond is quickly mixed, how long it would take to restratify by itself. As is evident from Figures 20 and 21, the pond regenerated its original temperature and density profiles in a period of less than one week and two weeks, respectively. Since the thermal diffusivity of a salt solution is significantly larger than its salt diffusivity, the temperature profile is modified much more quickly than the density profile.

In the second unmixing test, while there was some excess salt at the bottom of the pond, no special care was taken to make sure that the pond was fully saturated at all levels. In this test, the dilute and concentrated brine flow rates were initially set at 20 cc/min and 30 cc/min, but they later stabilized at 18 cc/min and 37.5 cc/min, respectively. At these flow rates the net circulation time for the pond between the two withdrawal ports (4 cm and 76.5 cm below the pond surface) was 3.6 days or 87 hours, which is about 3 times larger than that for the first unmixing test. Due to repeated salt precipitation in the dilute brine line, the test was stopped after about 80 hours, and the pond was allowed to unmix on its own. During this test, density profiles were taken at 5-hour intervals, while temperature profiles were taken at 1-hour intervals in

the beginning and then at 2-hour intervals. The density and temperature profiles before, at the end, 3 days and 14 days after the end of the test are shown in Figures 22 and 23, respectively.

As is evident from Figure 23, the temperature profile in the middle and lower levels did not change during the unmixing test. However, in the upper levels the temperature increased by about 4 to 5°C. On the other hand, the density profile had a uniform region between 35 and 70 cm before the mixing test began, as shown in Figure 22, indicating a convecting layer. This was primarily because the pond was slightly unsaturated between these two levels. When the pond mixing was stopped after 80 hours, the density in the bulk of the pond had decreased, and the uniform density region had increased by about 15 cm. Although the density in the bottom 15 cm had not changed, the density had increased in the top 20 cm.

During the two-week period (3/21/79 to 4/4/79) following the mixing test, the pond was allowed to unmix by itself. However, there was no significant improvement either in the density or the temperature profile as in the first unmixing test. Since the pond was not fully saturated to begin with, not only did it not unmix, but also its stratification deteriorated during this test.

b. Discussion

The first unmixing test on disodium phosphate conclusively demonstrated that if the pond is fully saturated at each level it can be used to unmix the mixed brine into dilute and concentrated brines. For this solute a residence time of about two weeks should be adequate. Based upon the results of the second unmixing test, it is also evident that if the pond is not fully saturated, due to the presence of a convecting layer (uniform in density) in the pond, a complete unmixing may not be achieved.

In general, the disodium phosphate pond was relatively easy to work with in the laboratory. Its density and solubility increased appreciably with temperature in the 25°C to 55°C range. For this reason, the pond stratified rather quickly in only three days. The only difficulty which we experienced with this pond was when the pond temperature dropped to near room temperature due to a power failure. This resulted in the complete "freezing" of the pond solution due to the formation of the hydrate. When the heater was turned on at 60°C, the pond did not heat up quickly because of the insulation provided by the solute around the heating coil. The temperature of the heating bath had to be increased to about 80 to 90°C to get the salt back into solution in a few days.

5. Potassium Alum Pond Tests

This pond was made of a polypropylene tank (2' x 4' x 3' deep) with a stainless steel bottom, as shown in Figure 3. The pond was heated by means of ten electrical heating tapes with a total energy output of 960 watts at 110 volts. The temperatures of the metal plate and the salt solution in the pond were monitored by a string of thermocouples. Some difficulty in getting a fully saturated pond was overcome by suspending cloth bags containing alum. One unmixing test of 22-day duration was conducted in this pond and is discussed later in this section.

Figure 24 gives the saturation temperature and density of saturated alum solutions as functions of anhydrous alum concentration in the alum solution. A comparison of laboratory data with the published literature is also shown in this figure.

a. Pond Stratification

i. First Attempt: Pond Layering with Excess Salt at the Bottom.

On 6/25/80, the pond was filled with three nearly saturated solutions at 60°C, 30°C, and 20°C to a total depth of about 85 cm. The total amount of hydrated alum $[K_2Al_2(SO_4)_4 \cdot 24H_2O]$ in these three layers was 123.3 Kg. The voltage variac was kept at 100% during the filling process.

The temperature profile right after filling showed a ΔT (the temperature difference between the bottom layer and the top layer) of about 40°C. On the evening of 6/25/80, the voltage setting for the heating tapes was lowered to 50%.

The temperature and density profiles at 1435 hours on 6/26/80 indicated that the pond was undersaturated throughout the depth. On 6/27/80, 20 Kg of alum were added in two installments, and the voltage setting was further reduced to about 40% for the weekend of 28 and 29 June. Unfortunately, no improvement was noticed in further saturation of the pond, even though there was plenty of undissolved salt at the bottom plate. Although the pond had very stable density and temperature profiles, it was not fully saturated, and for this reason, the unmixing test could not be conducted. It is quite true that if we had waited for a very long time (several weeks or months), the pond would have become saturated throughout its depth because of salt diffusion from the bottom layers.

ii. Second Attempt: Creation of Density Stratification from a Mixed Saturated Pond

On 6/30/80 it was decided to mix the pond solution thoroughly and heat it so that all the salt at the bottom and 22 Kg of additional alum (for a total of 165.3 Kg)* went into solution. During the mixing of the pond, it was discovered that the salt was "fused" to the bottom of the tank and had to be chipped off by a heavy sharp object. This salt layer at the bottom was providing insulation to the heat input by the heating tapes. This was confirmed by a very large difference between the temperature at the bottom of the metal plate and the solution temperature at the bottom of the tank. Secondly, different thermocouples fixed on the bottom side of the metal plate showed a temperature differential of as much as 42°C, principally because of an uneven salt layer thickness on the plate. However, once the salt was chipped and broken loose, the temperature differential dropped to less than 10°C.

*From Figure 1, it was estimated that the laboratory saturated pond with 25°C at the top and 60°C at the bottom would require about 165 Kg of hydrated alum.

The pond was uniformly heated to about 56°C (saturation temperature for the pond solution) by means of heating tapes. At this temperature, all the salt in the pond went into solution. Beginning at 0905 hours on 7/1/80, the pond was allowed to stratify on its own. However, during the next nine days, the pond did not stratify at all. On the contrary, it was probably convecting, as evidenced by uniform temperature and density profiles in the pond. During this period, the heat output from the heating tapes was gradually decreased, and a fan on the free surface was also provided to help cool the top layer, but nothing helped. The pond temperature gradually dropped from about 50°C to 30°C, but there was neither any significant precipitation of salt at the free surface nor any indication of density or temperature stratification. On the morning of 7/11/80, this test was stopped.

iii. Comments on the Above Two Tests

The following general observations were made in stratifying the laboratory alum pond using the two approaches described above:

1) The alum solution can be cooled several degrees Celsius below its saturation temperature without any salt precipitation. In other words, it takes a long time before salt starts precipitating from saturated solution.

2) Alum powder, when poured into a tank or when precipitating from the solution in a pond, sticks to the bottom of the pond, forming a thin crust, which in turn acts as a thermal barrier to any heat transport.

Because of 1) it was felt that alum solution may take a very long time to unmix into a dilute solution and a concentrated solution in a saturated solar pond.

Some difficulties were also experienced because of the use of electrical heating tapes at the bottom of the metal plate. Previously, we had been using a heat exchanger coil with constant-temperature heat bath for

heating of the pond. By using heat tapes, we had to develop a feel for how much heat input flux (watt/m^2) will correspond to a particular temperature at the bottom of the pond. This in turn depended upon the heat losses from the pond.

iv. Third Attempt: Pond Layering with Salt Bags

On 7/11/80 it was decided to stratify the pond again by layering it. The pond was filled with three layers at about 55°C , 40°C and 30°C . The voltage variac was set at 30%; i.e., the power output from the ten heating tapes was 9% of 960 watts* or 10.8 watt/ft^2 . While the temperature in the pond increased from the top to the bottom, the density increased only from 1.067 to 1.092. The pond was nearly saturated for the top quarter; it was undersaturated for the bottom three quarters. In order to provide more salt at the bottom layers, a cloth bag containing alum salt was suspended in the pond on the evening of 7/11/80, Friday. On the following Monday, 7/14/80, the pond consumed as much as about 20 Kg of salt and was nearly saturated at all layers. The density differential between bottom and top layer increased from (1.092 - 1.067) at 1700 hours on 7/11/80 to (1.1463 - 1.0710) at 0830 hours on 7/14/80. The temperature and density profiles on 18 July indicated that the pond was super-saturated at each level.

b. Brine Unmixing Test

Based upon the results of the unmixing tests on the disodium phosphate pond and the saturation density profile for alum solution, it was decided to conduct an unmixing test with lower flow rates. Consequently, on 21 July 1980, a brine unmixing test was run for a total of 22 days, from 21 July to 1 August, and then from 4 to 12 August. During this

*The power output from an electrical tape varies as the square of the voltage. At full voltage, the power output is $10 \text{ (tapes)} \times 96 \text{ (w/tape)} / 8 \text{ ft}^2 = 120 \text{ w/ft}^2$. At 30% voltage setting, the power output will be $(0.3)^2(120) = 10.8 \text{ w/ft}^2$.

test, dilute and concentrated brine flow rates of 35 cc/min each, were withdrawn from 10 cm and 77.5 cm below the pond surface, respectively. The mixed brine was returned at a level of 60 cm from the top surface. At a total brine withdrawal rate of 70 cc/min, the complete recirculation time for the entire pond (2' x 4' x 3' deep) was about 19.3 days. For this reason the test was run for 22 days, about 3 days more than one complete pond circulation. However, since the two brines withdrawn were from levels of 10 cm and 77.4 cm below the pond surface, for the region between these two levels the circulation time was only 14.5 days. Therefore, on this basis, which is more meaningful than the recirculation time for the entire pond, the pond was turned over about 1-1/2 times during the test period.

Several times during this test samples were withdrawn to actually measure the densities of different flow streams. Invariably, these were lower than the density measured in situ by the Troemner balance. While the difference was greatest for the concentrated brine stream, that for the dilute brine stream was within experimental error. Moreover, on 5 August 1980, apart from the center of the pond, density profiles were also measured near the two sides (with inlet and withdrawal ports) of the pond. It was found that generally these three profiles were within one-half percent of each other. Two to three times every day, the flow rates of dilute and concentrated brine streams were actually measured and if necessary adjusted to make sure that these were around the initial value of 35 cc/min. To maintain the pond temperature between 50 and 56°C, the heat output from the electrical tapes was increased by increasing the voltage from 30 to 35% in three steps during the duration of this test. However, it was observed that the temperature at the bottom of the pond was slowly decreasing.

The density and temperature profiles for this test are given in Figures 25 and 26 respectively. As is evident from these figures, the bulk of the pond, particularly between the levels of 10 and 77.5 cm, was completely mixed up as a result of this unmixing test. This proves that the residence time of 14.5 days for the alum saturated pond between 25°

and 55°C is not adequate. This is probably because the increase in saturation density of alum solutions between these two temperatures is only about 10 percent--this is not very large for a three-foot-deep pond based on sodium chloride solar pond data. During this test the temperature difference between the bottom and the top layers of the alum pond decreased from 28.5°C to 20°C primarily because the pond bottom temperature dropped by 6°C.

After running the unmixing test for 22 days, starting 14 August 1980, the pond was allowed to recreate the density stratification. In this period it was observed that the pond temperature at the bottom gradually dropped, which was corrected by increasing the voltage. During the following two weeks the pond did not show any appreciable improvement in the density profile even though the voltage was gradually increased from 35% to 45% in small steps. On 27 August it was decided to stop this test, and the pond was drained.

c. Material Compatibility Test

The bottom of the alum laboratory pond was made of stainless steel (Carpenter 20-cb-3). This material, although very expensive, was chosen because it was feared that the alum solution might attack aluminum and copper. A copper compatibility test was conducted for about one month. Under this test, a copper elbow of 12 mm ID and 15 mm OD was placed in 200 ml of saturated alum solution at 50°C by means of a constant-temperature bath. After more than three weeks, the test was stopped, and it was observed that there was no chemical attack to the copper tubing.

d. Discussion

The set-up for the alum saturated pond had all the good features which were developed during this contract. The actual unmixing test also went quite smoothly. Unfortunately, due to the chemical characteristics of alum saturated solutions, the pond stratification could not be easily self-generated, as evidenced by the pond stratification test (from

7/1/80 to 7/11/80) and the pond unmixing test (from 8/14/80 to 8/27/80). The alum solution takes too much cooling below its saturation temperature to release salt. Consequently, based upon the results of the unmixing test, it is estimated that the residence time for the mixed brine in the saturated pond must be more than 14 days. If the pond had been stratified from 25°C to 80°C or higher, its saturation density would have increased from 1.06 to 1.45 thereby making the pond very stable. Unfortunately, the density of an alum saturated solution increases from only 1.06 to 1.16 between 25 and 55°C. However, it was decided to run the alum pond test below 60°C to avoid cracking of the pond, which can occur at a higher temperature, as experienced earlier.

It would be very desirable to conduct one more unmixing test on the alum pond with a bottom temperature of about 80°C.

6. Evaluation of Other Solutes

In addition to the five solutes discussed above, several other solutes were also considered as possible candidates for a saturated solar pond. According to the limited solubility data in the published literature on sodium bisulfate (NaHSO_4), it may possibly be a promising solute for a saturated solar pond. However, our repeated test results were unable to confirm that the saturation density of NaHSO_4 solution in water increases with temperature. Therefore, this salt was not tested in a saturated pond.

On the suggestion of Mr. Eugene Kinelski, technical project officer for this contract, sulfites and sulfates of calcium, sodium, and potassium were also evaluated for saturated solar pond application. These salts are available as byproducts from different industrial chemical processes.

Based on published data in the literature, it appeared that potassium sulfate was the only one of these solutes which may be a possible candidate for saturated ponds. Its solubility, in grams of K_2SO_4 per

100 grams of water, increases from 11.1 at 20°C to 24.1 at 100°C. Since the solubility of K_2SO_4 does not increase sufficiently with temperature, it was not tested in the laboratory pond.

III. CONCLUSIONS AND RECOMMENDATIONS

The objective of this contract was to investigate the technical feasibility of using a saturated solar pond for brine unmixing. This was to be accomplished in the laboratory by demonstrating that (i) a saturated solar pond can self-generate and self-maintain a stable density stratification, and (ii) a stable stratified pond when mixed can recreate its stratification. Laboratory tests were also done to estimate the time required by a saturated pond to unmix a brine stream of intermediate concentration into dilute and concentrated brine streams. Based upon the experimental results, the following conclusions can be drawn:

1. Borax Pond - a one-foot-deep borax saturated pond can self-create and maintain a stable density stratification which can sustain a temperature gradient of about 0.6°C per cm without any external maintenance of the salt gradient or initial salt concentration stratification. Based upon the results of preliminary tests, it appears that the residence time for brine unmixing should be on the order of a few days.
2. Potassium Perchlorate Pond - Because of a very small increase in the saturation density, it was not possible to establish a stable potassium perchlorate pond.
3. Potassium Nitrate Pond - A saturated KNO_3 pond can self-generate a stable density profile, and can maintain stable density and temperature profiles by itself. It can regenerate itself after complete mixing. Results of 4-hour, 6-hour, and 8-hour heating and cooling tests have shown that a KNO_3 saturated pond is capable of recovering by itself. Based on a solute precipitation test, it was observed that KNO_3 did not precipitate even after three days when the pond temperature was 3°C below its saturation temperature. KNO_3 did precipitate when the pond temperature dropped about 8°C below its saturation temperature.
4. Disodium Phosphate Pond - Two unmixing tests were conducted on this pond. The first test conclusively demonstrated that if the pond is fully saturated at each level, the pond residence time for brine unmixing should be about two weeks. The second unmixing test demonstrated that if the pond is not fully saturated a complete unmixing may not be achieved even if the pond has a stable density stratification.

5. Potassium Alum Pond -An alum solution can apparently be cooled by as much as 20°C below its saturation temperature without any significant solute precipitation. Due to this characteristic, a stable alum pond stratification could not be established from a mixed pond. However, it was possible to establish a stable saturated pond by suspending salt bags in the pond. The pond unmixing test was conducted between 25°C and 55°C. For this temperature range, the pond residence time for brine unmixing should be more than two weeks. However, it should be possible to have a residence time of two weeks or less if the pond bottom temperature is about 80°C. The saturation density increase from 25°C to 80°C is 1.06 to 1.45 as compared to only 1.16 for the saturation temperatures of 25°C to 55°C. It is recommended that one more alum pond unmixing test with the top and bottom temperature of about 25°C and 80°C should be undertaken.

IV. REFERENCES

1. InterTechnology/Solar Corporation, "Review of the Current Status of Reverse Electrodialysis Systems for Salinity Power Systems Using a Stratified Saturated Solar Pond," Report No. 220280 to the U.S. Department of Energy, February 1980.
2. Ebasco Services Incorporated and InterTechnology/Solar Corporation, "Preliminary Design of an Osmotic-Type Salinity Gradient Energy Converter - Phase II. Saturated Solar Pond System," Report to the U.S. Department of Energy under Contract No. DE-AC05-79ET-21001, August 1980.
3. InterTechnology/Solar Corporation, "Saturated Solar Ponds for Energy Collection," Report No. 030380 to the Jet Propulsion Laboratory for the U.S. Department of Energy, March 1980.

Figure 1. Schematic diagram of circular plastic pond

Figure 2. Schematic diagram of rectangular plastic pond

Figure 3. Schematic diagram of rectangular plastic pond with metal bottom

Figure-4. The details of the arrangements used for the unmixing test.

Figure 5. Solubility and density of saturated borax solutions in water

Bath temperature from 2 to 20 February 1979 was maintained at about 150°F (66°C)
 For temperature scale: 100°F = 37.8°C and 150°F = 65.6°C
 ΔT = (Pond bottom temperature - thermocouple 16)

Figure 6. Temperature distribution in borax saturated pond during second self-generation test

Figure 7. Borax pond regeneration after mixing on 2/21/79

Figure 8. Solubility and density of saturated potassium perchlorate solutions in water

Figure 9. Solubility and density of saturated potassium nitrate solutions in water

* The change in ΔT reflects the changes in ambient temperature
 ΔT = Bottom temperature - surface temperature

Figure 10. Temperature distribution in potassium nitrate saturated pond during initial stratification

Figure 11. Single-cycle cooling test, heating off 4 hours, heating on 4 hours

Figure 12. Representative cycle for the 4-hour cooling and heating test (6th cycle)

Figure 13. Overall temperature variation during the 4-hour cycling test

Figure 14. Representative cycle for the 6-hour cooling and heating test (9th cycle)

Figure 15. Overall temperature variation during the 6-hour cycling test

Figure 16. Representative cycle for the 8-hour cooling and heating test(5th cycle)

Figure 17. Overall temperature variation during the 8-hour cycling test

Figure 18. Modification of temperature profile due to cycling test

Figure 19. Solubility and density of saturated disodium phosphate solutions in water

Figure 20. Density profiles during the first unmixing test

Figure 21. Temperature profiles during the first unmixing test

Figure 22. Density profiles during the second unmixing test

Figure 23. Temperature profiles during the second unmixing test

Figure 24. Solubility and density of saturated potassium alum solutions in water

Figure 25. Density profiles during the unmixing test

Figure 26. Temperature profiles during the unmixing test