New Uses of Solar Energy

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ABSTRACT

Production of saline minerals is made possible by utilizing new solar pond technology. Temperatures in excess of 200°F can be generated by absorbing the sun's energy in a salt solution. Low temperature chemical reactions are carried out in the solar pond to produce the following saline minerals in the crystalline form:

- *Anhydrous sodium sulfate*
- *Magnesium sulfate monohydrate*
- *Sodium carbonate monohydrate*
- *Sodium borate monohydrate*

Other uses of solar energy are also possible as follows:

- *Waste management*
- *Brine deposit enrichment*
- *Hot solution mining*
- *Salting out processes.*

These new uses of solar energy are of vital importance in light of the increasing cost of fossil fuel.

INTRODUCTION

Although the mechanism of heating within the solar pond was observed as a natural phenomenon just after the turn of the Twentieth Century, it was not until 1954 that two Israeli scientists, Rudolph Bloch and Harry Tabor, proposed that the principle be evaluated for commercial applications. The use of artificial salt-gradient ponds was envisioned as a means of providing thermal energy to heat buildings, to provide industrial process heat, and to generate electricity. An initial test pond with an area of 600 m^2 was built in 1960 and attained a temperature of 95°C, proving that the concept worked. In the 1970s, several ponds were built in the U.S. with the research efforts aimed at various aspects of the emerging technology.

The Israeli solar pond program has probably progressed the farthest toward commercialization. A 1100-m^2 pond built in 1975 near the Dead Sea Potash Works captured a reported 15% of the incoming solar radiation, with the pond's bottom temperature reaching 103°C. Ormat Turbines operated a 1400-m^2 pond at Yavne for use in generating electricity. This pond provided hot brine from its storage layer at 90°C to the boiler of an organic Rankine-cycle turbine. The world's largest pond, covering 7000 m^2, was completed in 1978 at the Ein Bokek. Brine from the pond has been used to drive a turbine producing 35 kilowatts of electricity on a continuous basis with a peaking capability of 150 kilowatts. A primary focus has been the development of large-scale base load electrical generation in the Dead Sea, possibly using water from the Mediterranean.

In the United States, probably the best known attempt at developing a similar project has been at the Salton Sea in Southern California. However, the brine concentration at the Salton Sea is only about 3.5% salt, requiring extensive ponds to achieve appropriate brine concentration. It is reported that fragile project economics as well as environmental concerns have resulted in a cessation of activities at this location. Alternate sites are being evaluated for siting a 5-MW and possibly a 20-MW facility at the present time.

Most of the approaches toward recovering solar energy as low-level thermal energy continue to be plagued with uncertain economics. Experimental work essentially ceased from 1966 to 1974 because conventional energy was so inexpensive. The energy crisis resulted in rejuvenation of many research programs. However, the current economic conditions coupled with the purported relaxation of the energy crisis has resulted in cutting back or dropping projects that are funded either privately or wholly or in part by the government. Projects with high cost/benefit ratios that were included in programs for the sake of amassing knowledge are being dropped because of budgetary constraints. Many solar developments, including solar ponds for electrical generation, continue to be partly dependent upon state and federal tax credits.

The most attractive solar application for private industry will almost certainly include relatively low process temperature requirements coupled with a geographic location that exhibits favorable meteorological conditions. Salt and mineral processing involving chemical transformations which occur at temperatures well within the ranges attainable in solar ponds merit thorough investigation. Thermal efficiencies should be reasonably high, well above the 1–2% conversion to electrical energy experienced in the ponds aimed at power generation.

A process for the production of anhydrous sodium sulfate, sodium carbonate monohydrate and other minerals was devised and patented under U.S. Patent No. 4,179,493, "Dehydration Process." A sodium sulfate demonstration pond system was built in Turkey and operated solely for producing anhydrous sodium sulfate. This process, involving a pond required to reach a minimum of 32°C, appears to be a practical means of producing the chemical much less expensively than via conventional means. The purpose herein is to review the potential application of this technique to the processing of minerals which exhibit crystal transformations, primarily dehydration, in the temperature ranges attainable in saturated solar ponds, but not attainable in conventional evaporation ponds. This investigation involves the processing of sodium carbonate in a 400-m^2 solar pond at Owens Lake, California.

TYPES OF SOLAR PONDS

Salt gradient solar ponds exhibit, as the name implies, a density gradient in which the density at the surface is less than the density at the bottom. Normally the pond has three distinct layers, as indicated in Figure 1. The upper and lower layers are homogeneous and convective, while the middle layer is non-convective. While the brine in both of the convective zones is continuously turning over, the fluid in the non-convective zone is gravitationally stable. A density gradient, wherein the lower layers within the zone are more dense than the upper layers, keeps the mixing to a minimum. Because the layer is non-convective the transfer of heat through the gradient layer to the surface can only occur by conduction. This process is relatively slow, with the gradient layer acting as an insulator.

The common reference to a salt-gradient solar pond involves a non-saturated condition in all or most of the pond. In cases where the capture of heat in the lower convective layer is the prime objective, for example in ponds for electrical generation, none of the pond needs to be saturated. All that is required is that the concentration gradient across the non-convective zone be adequate to ensure the stability of the zone. Establishing an unsaturated

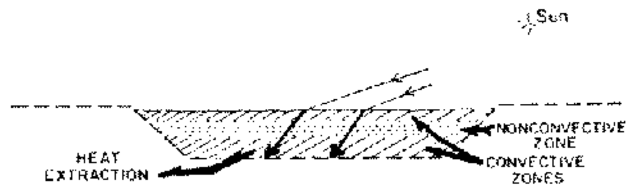

Figure 1. Distinct Layers of a Solar Pond.

salt-gradient solar pond requires a careful approach. After placing the homogeneous lower convective layer, a number of layers of brine with decreasing gravity must be added successively into the pond. Finally, a layer of fresh water is placed on top as the upper convective zone. Diffusion of salt across the layer boundries is a problem and will lead to the eventual loss of the gradient layer if careful maintenance is not carried out.

A saturated solar pond is one in which all of the layers are saturated. This concept is somewhat limited by the required utilization of only those salts which exhibit fairly sizeable increases in solubility with temperature. The lower layers, being at a higher temperature than the layer directly above, will contain more salt and consequently be at a higher density. The pond becomes essentially self-regulating as the temperature gradient maintains the salinity gradient. Diffusion is not a problem and little maintenance of the pond layers is required, or possible for that matter.

A brief comment concerning the origin of the convective layers seems appropriate. The theoretical diurnal temperature profile is illustrated in Figure 2a. However, the intense solar radiation during the day will result in a temperature buildup at the surface as well as at the pond bottom. This buildup results in temperature gradients which exceed the limits of density stability, resulting in the formation of both the upper and lower convective zone.

Temperature profiles similar to Figure 2b will result.

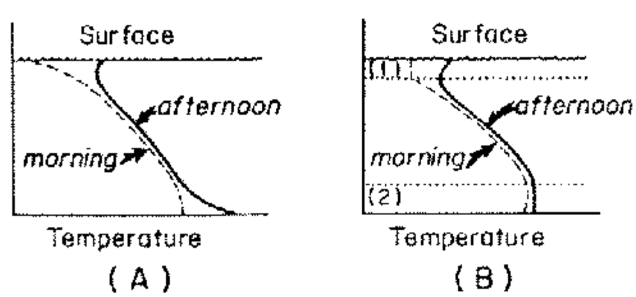

Figure 2a. Theoretical Diurnal Temperature Profile.

Figure 2b. Temperature Profiles Resulting from Intense Solar Radiation.

OWENS LAKE APPLICATION

Owens Lake is one of the world's largest surface deposits of trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, the raw material mineral for natural soda ash production. Conventional technology includes the evaporative crystallization of $Na_2CO_3 \cdot H_2O$, sodium carbonate monohydrate, a step that requires a significant input of thermal energy.

The utilization of solar energy to accomplish this dehydration merits evaluation, because the Owens Lake location in the high desert of eastern California exhibits quite high insolation rates. Figure 3 compares the mean daily solar radiation values for various locations in the United States. The Inyokern, California data is slightly higher than at Owens Lake; however, it is used as a comparison because of the availability of data from the China Lake Naval Weapons Center.

PHYSICAL CHARACTERISTICS OF THE TEST POND

The surface area of the experimental pond was fixed at 400 m^2 primarily because of previous experience with the aforementioned sodium sulfate pond in Turkey. This size was felt to be adequate to ensure that the edge effects, where added heat losses can occur, would not materially affect the data obtained. Another consideration was that the area be large enough to avoid the formation of a complete crystalline layer on the surface, a phenomenon that occurred in all of the laboratory efforts to simulate a solar pond. Although the experimentation is far from complete, the initial observations are that 20 × 20 meter size is adequate to accomplish these objectives.

The pond was constructed on a sand base, with clay mixed with the upper sand surface to allow reasonable compaction. A sprayed asphalt liner was applied to the surface; this type of liner was selected as an added part of the evaluation. A concrete weir arrangement was constructed through the berm to allow drainage of the pond and to control decantation of the surface brine.

AVERAGE INSOLATION RATES

(Langelys = g-cal/cm^2)

Spokane, WA	361
Boise, ID	395
Great Falls, MT	366
Las Vegas, NV	509
Phoenix, AZ	520
El Paso, TX	536
Inyokern, CA	568

Figure 3. Comparison of Mean Daily Solar Radiation Values (U.S.)

MINERAL PROCESSING OBJECTIVE

Sodium carbonate solubility with respect to temperature is included as Figure 4. The solid phase in equilibrium with saturated solution from about −2°C to 31°C is the decahydrate, $Na_2CO_3 \cdot 10H_2O$. An intermediate hydrate, $Na_2CO_3 \cdot 7H_2O$, is stable from 31°C to about 36°C. $Na_2CO_3 \cdot H_2O$, sodium carbonate monohydrate, is the solid phase up to about 105°C.

By feeding a solar pond with a sodium carbonate solution that is at or near saturation, any cooling within the upper layers and/or evaporation at the pond surface will result in the crystallization of $Na_2CO_3 \cdot 10H_2O$. The crystals formed, being more dense than the solution, will sink through the upper layers, encountering temperatures that equal or exceed the transition temperature. Melting should occur and be followed by the crystallization of the stable crystal, $Na_2CO_3 \cdot H_2O$. The waters of hydration that are released still hold a substantial amount of Na_2CO_3 and constitute a saturated solution. This solution is displaced upward by the crystals that are settling, with the saturated solution quickly encountering the lower temperatures, and crystallization of decahydrate again occurs. Recycling of the upper layers to the feed preparation station allows control of the soluble impurity levels in the pond and provides proper maintenance of the pond water balance. Water addition must match the surface evaporation plus the content of the stable $Na_2CO_3 \cdot H_2O$ that is formed.

MATERIAL AND ENERGY BALANCE

The material and energy balances presented herein are based on theoretical calculations that incorporate generally accepted practices established by other researchers in the solar energy field. The meteorological information is primarily historical data, adjusted to the Owens Lake location. The collection of operating data from the test pond only has begun at this point. Initial observations tend to confirm assumptions made in the material and energy balances; however, the balances should not be construed as being confirmed by data. Details of an energy balance felt to be representative of spring meteorological conditions are given in Figure 5.

The incoming radiation falls within both the short and long wave spectrums. Short wave, also known as extraterrestrial or solar radiation, falls between 0.3 and 3 microns and is capable of penetrating the surface of a pond. It therefore plays the more significant role in heat accumulation and provides the energy for utilization. Long wave radiation, considered to be in the 3- to 100-micron range, does not penetrate the upper surface layer. The pond surface radiates long wave energy back to the atmosphere, the energy representing a large percentage of that leaving the pond.

In this specific example, the 380 w/m^2 of short wave radiation represents a typical May value. The long wave

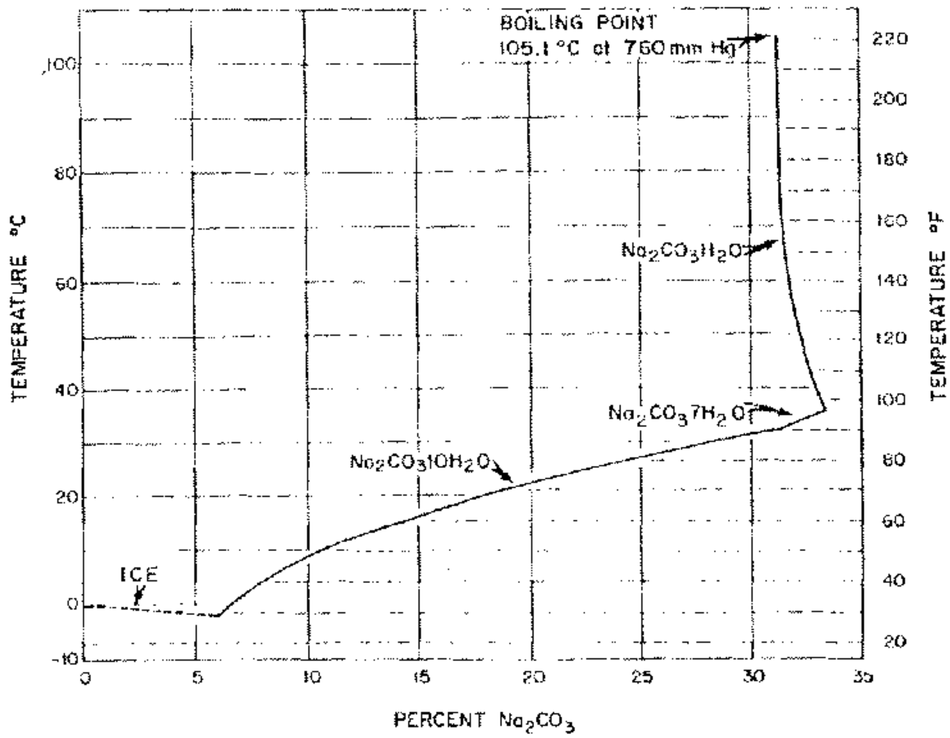

Figure 4. Sodium Carbonate Solubility with Respect to Temperature.

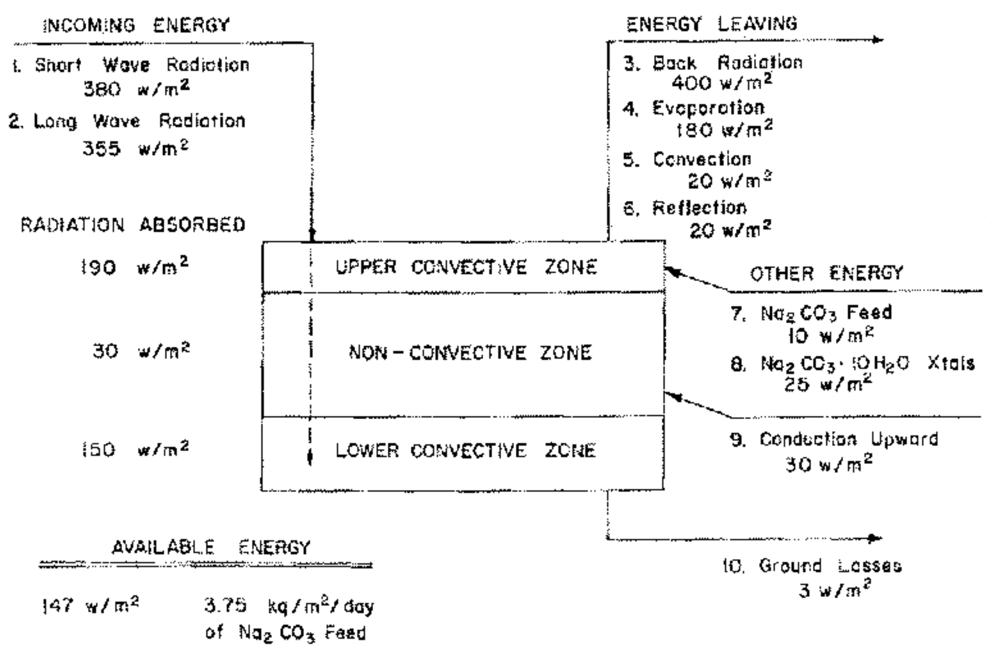

Figure 5. Typical Energy Balance.

value of 355 w/m² is a measured value for a similar time of the year. The long wave value is related to the ambient temperature and the cloud cover.

The radiation absorbed in the three layers is derived through use of experimental data which reflects the actual absorbency of seawater. The relationship of the fraction of the energy transmitted (T) versus the depth (Z) in meters is of the general form:

$$T = a + b \ln (Z)$$

with $a = 0.36$ and $b = 0.08$ being used for these estimates. The transmitted values are multiplied by 0.80 to allow for any reduction in transparency of the pond.

Back radiation represents the largest quantity of energy leaving the pond surface. This value is calculated through use of the Stefan-Boltzmann equation for black body radiation. The major variable is the temperature of the surface with radiation varying in terms of the fourth power of the absolute temperature. The evaporation loss of 180 w/m² is equivalent to the surface evaporation of 0.25 inches of water per day which is based on available data from the location.

Convective losses were calculated through use of the Bowen ratio, which relates the sensible heat loss and the heat loss due to evaporation. This ratio is a function of the temperature differential between the brine at the surface and ambient temperature and the difference between the vapor pressure of the brine and the air at the surface. Added data indicates the sensible heat loss to be about 10% of the evaporative loss, thus giving fairly good confirmation of the Bowen ratio calculation.

Reflective losses are estimated to be 20 w/m², an albedo of 3% of the total incoming radiation being used.

The sodium carbonate plays a significant role because of energy entering with the feed material and through heat evolved by the crystallization of the decahydrate. The 10 w/m² representing the sensible heat of the feed and the 25 w/m² resulting from the crystallization have been added to the upper convective zone.

The gradient layer contributes to the energy being provided to the upper convective layer. The heat conducted upward through the non-convective layer was discussed previously, since it is the measure of the effectiveness of the insulating gradient layer. The calculation is represented by (k)dt/dz, where (k) is the thermal conductivity of the brine and dt/dz is the temperature gradient in the non-convective zone. Experience with this pond has indicated dt/dz to be about 50°C/meter. Using a brine conductivity of 0.6 w/m °C, the energy conducted upward to the top layer becomes 30 w/m². This value is the same as the energy absorbed into the layer, indicating a zero net flow of energy within the gradient layer.

The overall energy balance pertaining to the upper convective layer thus contains the following values:

IN		OUT	
Short Wave Radiation	380 w/m²	Back Radiation	400 w/m²
Long Wave Radiation	355	Evaporation	180
Upward Conduction	30	Convection	20
Decahydrate Crystallization	25	Reflection	40
Sensible Heat in the Feed	10	Transmission	180
	800 w/m²		800 w/m²

The balance within the lower layer then leaves a net of 147 w/m² for the crystallization of $Na_2CO_3 \cdot H_2O$, this energy representing about 39% of the available short wave radiation striking the pond.

SUMMARY

A dynamic computer model that simulates the diurnal changes has been prepared and is being refined as additional data become available. As previously mentioned, more experimental work is required to quantify the many variables affecting this solar pond application. The processing of minerals in solar ponds does appear to be a practical application of solar energy based on data available at this time.

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