

# Advances in Solar Salt-Solar Evaporation in Multicomponent Processes

Mauritz J. Kallerud

Garrett Research and Development Company, Inc.  
1855 Carrion Road  
La Verne, California

## ABSTRACT

*The use of solar evaporation to dewater and concentrate raw materials from multicomponent brine systems is reviewed. Economical refining processes can be based on harvested solar salts, as shown by expanding worldwide production. Test work on the brines recovered from Searles Lake, a very rich, but complex reserve, is illustrative of the advanced technology that can be used in multicomponent systems.*

*More than 400 acres of prototype test ponds have been constructed to study the full-scale production of potash, borax, salt cake and soda ash at Searles Lake. Computer methods have been developed to study the evaporation and seepage rates of these ponds. The design, construction, and operation of evaporation ponds is critical in obtaining good pond performance and in the feasibility of using solar evaporation in complex chemical production.*

## INTRODUCTION

Solar evaporation processing has been profitably used for salt production for millennia, but most other uses of solar evaporation for saline recovery were too complex for feasible applications. However, modern technological advances have now reached a state that solar techniques may also be considered in many complex, multicomponent recovery operations.

There are presently several operational examples of economical uses. Perhaps the oldest modern examples are the potash production at the Dead Sea and at Bonneville, Utah. The newest, for the production of potassium sulfate, salt cake, magnesium

and lithium salts at the Great Salt Lake, is presently under construction. The best example of an unlimited future area is for the recovery of numerous coproducts from seawater (Garrett, 1969; Kallerud and Chemtob, 1967). At present, this area is limited almost exclusively to the production of halite, with millions of tons marketed annually. There is only token production of the more valuable ocean salts. Numerous other raw material reserves may also be well-suited to solar processes; for example, the complex but very valuable brines at Searles Lake, which have been studied extensively by the Garrett Research and Development Company, Inc., a subsidiary of the Occidental Petroleum Corporation. These operations are being organized under the Searles Lake Chemical Corporation, also a subsidiary of Occidental.

## HISTORY OF SEARLES LAKE

The age of Searles Lake has been estimated at 875,000 years or perhaps older. Salts have been deposited in the Lake as a series of horizons in the Pleistocene epoch. The earliest saline deposits of the Sangamon (or perhaps Yarmouth) age are composed of halite, trona and nahcolite. The next, Early Wisconsin in age, is primarily mud with gaylussite. The most interesting and well-studied deposits of Middle Wisconsin and Early Recent age contain primarily halite, trona, borax, hanksite and burkeite. These units that are presently being mined are the upper and lower ore bodies, dated at 33,000 years B.P. The final halite and mud mixture on the surface of the Lake was formed during the Late Recent age. The formation of these deposits was associated with the filling and lowering (evaporation) at the Lake due to past glacial events.

The processing at the Lake is based on the pumping of saturated brines from wells in the ore body. These brines are partly the original Pleistocene brine in equilibrium with the crystalline deposit. Continued mining has depleted much of the original brine. A reconstituted brine is continuously formed by the leaching of the deposit with rainwater and runoff, but the composition of this new saturated brine does not reach that of the original brine, especially in its potassium concentration.

At present, potassium chloride, soda ash, salt cake, and boron products are being produced by the American Potash and Chemical Corporation and the Stauffer Chemical Company. Processing is based on combinations and variations of plant evaporation, carbonation, cooling-crystallization and extraction. A certain amount of solar evaporation has been used recently to preconcentrate brines before plant evaporation, but the only other significant process change in recent years is the use of solvent extraction in boric acid production. The Garrett Research and Development Company has undertaken the task of applying the most advanced techniques of solar evaporation, in combination with economical phase separations, to expand the development of Searles Lake and to economically process the newly reconstituted Lake brines.

### PROCESS DESCRIPTION

The technology of a Searles Lake solar operation might first be compared to the operational example of halite solar systems and their raw material supplies; the sequencing of ponds for preconcentration, storage and crystallization; and product harvesting, washing, shipping, and marketing. These operations are based on long experience by competent producers, yet even with this background, it is a major task to initiate a new operation.

A proposed operation must meet the general requirement of a successful solar process before testing is even considered. Raw materials, usually as brines, are an initial requirement. In some cases, where the supplies may be limited, an extensive prospecting program is required. In other cases, such as in a seawater operation, this is not a problem.

At Searles Lake, a major portion of the known ore body is controlled by other operators. Therefore, an extensive exploration program was undertaken, under new Sodium Prospecting Permits, to define the extent of the upper ore body. It was

possible to prove that vast reserves of brine and salts were present in new areas that had not previously been tested. In Figure 1, the approximate limits of the new ore body discoveries are compared with the formerly recognized limits. Quality brines were pumped from many of the test wells at hundreds of gallons per minute. Present operators are satisfied with production flow rates as low as fifty gpm.

The second major requirement of solar processes is utilization of the proper land area. The U.S.

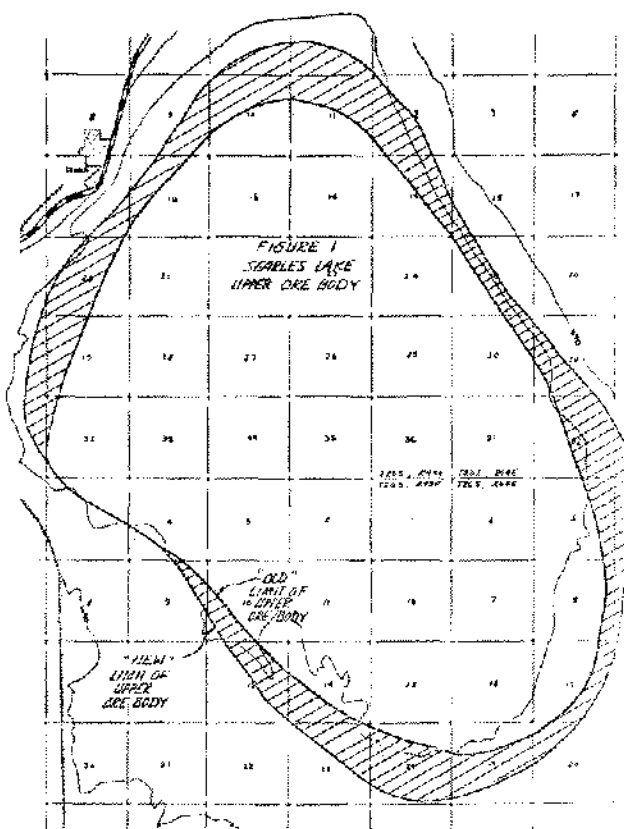


Figure 1. Searles Lake upper ore body.

Geological Survey topographical maps of Searles Lake show extensive areas that could be of real interest, so more detailed surveys were justified. It is necessary to know the exact topography as well as the natural construction materials in the area. An economical pond construction is most feasible when the land is flat or has an elevation gradient of less than ten feet per mile, so that ponds of fifty to several hundred acres can be constructed.

Fortunately, detailed mapping can be done at a cost as low as \$400 per square mile for large areas of 20 to 100 square miles, by using aerial photography with the proper ground controls. The plots can show contours at one-foot intervals to an accuracy of about six inches for this type of survey. If the land is too rough for mapping at one-foot contour intervals, it is also too rough for solar ponds.

Mapping of the site soil structure is of equal importance in the economic feasibility estimates. Cores or cuttings from drilling to depths of as much as 20 or 30 feet, but more typically to 10 feet, must be studied. When the materials for proper dike construction (Garrett, 1965a) are not immediately available at the location of the dike, they can often be hauled economically as much as a mile. Ponds with dikes costing up to \$1.00 per cubic yard can often be economically attractive.

After these first stages of survey and mineral evaluation have been successfully completed, the engineering and chemistry of a proposed operation can be properly evaluated. Production would be based on the processing of saturated Lake brines having six major ionic components: sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), tetraborate ( $\text{B}_4\text{O}_7^{=}$ ), sulfate ( $\text{SO}_4^{=}$ ), carbonate ( $\text{CO}_3^{=}$ ), and chloride ( $\text{Cl}^-$ ), as well as the two acid radicals of tetraborate and carbonate, namely, metaborate ( $\text{B}_2\text{O}_4^{=}$ ), and bicarbonate ( $\text{HCO}_3^-$ ). There are also a number of minor components such as sulfide ( $\text{S}^{=}$ ), lithium ( $\text{Li}^+$ ) and tungsten (W). Seawater in comparison contains only five major ionic species.

The solubility relationships in this brine have been well-documented by Teeple (1929). The solar concentration of the brine produces a series of crystalline products as the brine compositions advance to new crystallization fields. A typical brine would first crystallize halite ( $\text{NaCl}$ ) and burkeite ( $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$ ). Variations of the original brine compositions could also produce the crystallization of salt cake ( $\text{Na}_2\text{SO}_4$ ) or trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), usually in smaller amounts, before the crystallization of burkeite.

Continued evaporation advances the brine to a second major crystallization field with a mixture of halite, glaserite, borax, and additional burkeite. A third and final major field includes the products of halite, sylvite (KCl), glaserite, thermonatrite ( $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), borax, and some teepleite ( $\text{Na}_2\text{B}_2\text{O}_4 \cdot 2\text{NaCl} \cdot 4\text{H}_2\text{O}$ ). Teepleite is a very unusual double salt that is rarely encountered; however, its behavior in solar processing has been documented by Mr. Elie Chemtob, Manager of Chemical Research at the Garrett Research and Development Company.

The general behavior of the solar process can be followed schematically on a solubility diagram for the system  $\text{NaCl-KCl-Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-H}_2\text{O}$  at  $35^\circ\text{C}$  (see Fig. 2). Borax is not included as it would add another dimension to the diagram. Further, it is the most independent variable in the system and is at lower concentrations, so its interactions with the other components are evaluated separately.

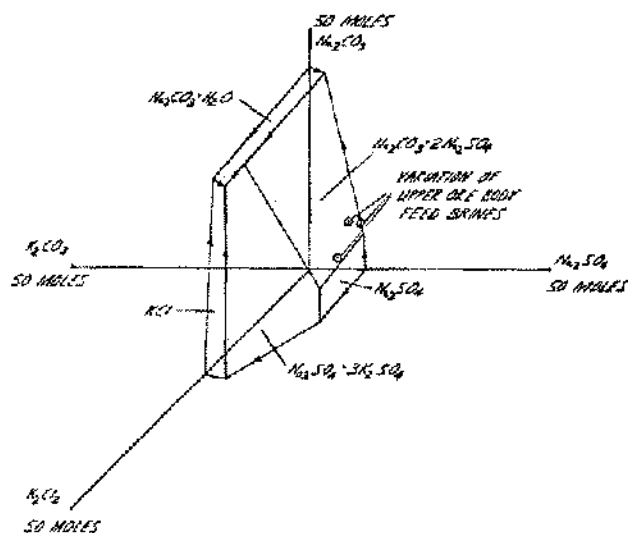


Figure 2. NaCl-KCl-Na<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O system at 55 °C. Basis: Moles per 1000 moles H<sub>2</sub>O.

Three different extremes of brine compositions that were found in the prospecting tests are also shown in Figure 2. These brines seem different in composition, but it can be seen that all are in the same area of the diagram and will follow similar solar evaporation paths.

The exact behavior of the brines is more complicated than indicated in the 35°C system because of varying meteorological conditions throughout the year. Winter cold and day-night temperature variations produce solubility changes and different crystalline phases. Cooler temperatures cause a lower concentration of potassium at glaserite saturation and, consequently, an earlier crystallization of glaserite. Borax solubilities are also reduced. The colder winter temperatures also cause the crystallization of glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and natron

( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ). Consequently, a summer operation when evaporation rates are highest is often preferred, as more uniform and larger quantities of solar crystallization products are formed.

The solar harvest intermediates are first handled as in a well-designed solar halite operation (Garrett, 1965b), including harvesting, handling and washing of the salts. The three main harvests of raw materials are processed in separate, but integrated streams to achieve the most economical and efficient operation. For example, the first harvest is about one-third burkeite which can be processed to soda ash and salt cake by one of several methods. Fractional crystallization can be used when low yields are acceptable, but processes including carbonation, cooling-crystallization, and solar or plant evaporation can increase yields to almost 100%. Most of these processes are well-known and do not require a detailed test evaluation in the preliminary studies.

The second and third types of harvests present very interesting sources of potassium and boron, and several unique processing methods have been developed for the separation and purification of both components at high yields. Details of the processes must be held as confidential until the patents are issued.

### EVAPORATION AND POND PERFORMANCE TESTS

The overall process feasibility based on land, minerals and processing can be evaluated at this point, although several additional factors, such as evaporation efficiency, must also be considered. Marketing, of course, is of paramount importance and must be considered separately.

Evaporation estimates and preliminary evaluations from the published literature are valuable, but the final results are dependent on field tests. The first construction of small solar test ponds was scheduled in late 1966 and full operations were maintained through 1967 and 1968. Harvest salts were also recovered from the first ponds for pilot plant testing. The data and experience from these operations were applied to the design of a larger-scale prototype test operation to collect full-scale operational data on the complex system.

Operations were scheduled to test the brine phase chemistry (as discussed earlier), wave action and pond operational characteristics, and the evaporation and leakage rates. Evaluation and correlation of evaporation rates have been the subject of numerous publications (Ferguson, 1952; Bony-

thon, 1966; Manker, 1967). The collection and evaluation of evaporation and seepage data from large test systems will be discussed in this paper. The larger test systems are preferred for obtaining good, full-scale test data, but they are also more difficult to accurately control. Measurement of brine concentration must be based on a composite sample to obtain an accurate determination of the content of a pond. Brine level or volume measurements must allow for the effects of the wind, since level variations from several inches up to a foot can occur at one data standpipe. Two standpipes per pond on the proper wind vector and fulcrum are a minimal requirement, but four, or even a fifth in the center, are preferred. The brine level measurements are taken on the inside of the perforated standpipes where the levels are steady.

The data can be evaluated by either of two preferred methods, using computers to expedite the digestion of data. Both methods of calculation are based on the comparison of total brine inventories and total tracer inventories. The brine must be accurately analyzed for a valid chemical tracer to determine the tracer inventory in a pond. The first calculation method is based on the direct determination of the leakage from the conservation of tracer inventory, with the evaporation determined by the difference in total volume inventory. In the second method, the evaporation is the relative change of tracer concentration in a given volume, with the leakage determined by difference from the total volume change. The equations used in these calculations are shown in Tables 1 and 2, respectively. The volume or thickness of crystallized salts must be included in both calculations, as it is part of the standpipe brine depth and volume measurement and can cause a serious error in the relative volume and tracer inventories. These salts may be estimated, as a ratio to evaporation, or can be surveyed. The final equations shown include the salts as a ratio factor, which must be confirmed by a later survey.

The two methods are directly applicable under all static, no-flow operating conditions, although corrections for cumulative inventory changes caused by pumping can be included. When the evaporation rates are low, as in the winter, the most accurate results are usually obtained using the second method, where evaporation is based on the relative change of tracer concentrations. The first method is more general, however, and applies to the more common case where evaporation is much greater than leakage. Both methods have been used at Searles Lake and were found to be reliable.

TABLE 1  
SOLAR PERFORMANCE CALCULATIONS

METHOD 1: Leakage as a Function  
of Relative Tracer Inventory

GIVEN:

$$S_{n,n+1} = C E_{n,n+1}$$

$$V_n = V_t - \sum S_{0,t}$$

$$V_{n+1} = V_{t+1} - \sum S_{0,t} - \sum S_{n,n+1}$$

THEN

$$L_{n,n+1} = \frac{V_n P_t T_t - V_{n+1} P_{t+1} T_{t+1}}{A [(t+1) - t] \left[ \frac{P_t + P_{t+1}}{2} \right] \left[ \frac{T_t + T_{t+1}}{2} \right]}$$

$$E_{n,n+1} = \frac{[V_t - \sum S_{0,t}] P_t T_t - [V_{t+1} - \sum S_{0,t} - \sum S_{n,n+1}] P_{t+1} T_{t+1}}{A [(t+1) - t] \left[ \frac{P_t + P_{t+1}}{2} \right] \left[ \frac{T_t + T_{t+1}}{2} \right]}$$

$$E_{n,n+1} + L_{n,n+1} = \frac{V_n - V_{n+1} + \sum S_{n,n+1}}{A [(t+1) - t]}$$

THEREFORE

$$E_{n,n+1} = \frac{1}{1-C} \left[ \frac{V_t - V_{t+1}}{A [(t+1) - t]} - L \right]$$

$$L_{n,n+1} = \frac{[V_t - \sum S_{0,t}] P_t T_t - [V_{t+1} - \sum S_{0,t} - \sum S_{n,n+1}] P_{t+1} T_{t+1} + \frac{C}{1-C} [V_t P_t T_t - V_{t+1} P_{t+1} T_{t+1}]}{A [(t+1) - t] \left[ \frac{P_t + P_{t+1}}{2} \right] \left[ \frac{T_t + T_{t+1}}{2} \right] + \frac{C}{1-C} \left[ \frac{P_t T_t + P_{t+1} T_{t+1}}{2} \right]}$$

Accuracies within hundredths of an inch per day are possible.

PROTOTYPE POND CONSTRUCTION  
AND OPERATION

Optimistic feasibility studies on the overall project were a basis for the continued and expanded tests on the Lake. A series of six prototype ponds were designed for full-scale operational tests. These ponds, covering 420 acres, were constructed and in service in less than one year from the date of the contract award.

Brine was supplied to the ponds through a 24-inch pipeline from the wells, more than a mile away. Each of the well pumps was run by a 24 hp diesel engine. Brine flow within the ponds was accomplished by gravity with weir control, except for one pond which was charged by pumping.

The ponds have been in service for almost a year and have been operating smoothly. Wave action,

TABLE 2  
SOLAR PERFORMANCE CALCULATIONS

METHOD 2: Evaporation as a Function  
of Relative Tracer Concentration

GIVEN:

$$S_{n,n+1} = C E_{n,n+1}$$

$$V_n = V_t - \sum S_{0,t}$$

$$V_{n+1} = V_{t+1} - \sum S_{0,t} - \sum S_{n,n+1}$$

THEN

$$E_{n,n+1} = \frac{V_n - 0.5 [V_n + V_{n+1}] \frac{T_t}{T_{t+1}}}{A [(t+1) - t]}$$

$$L_{n,n+1} + E_{n,n+1} = \frac{V_t - V_{t+1} + \sum S_{n,n+1}}{A [(t+1) - t]}$$

THEREFORE

$$E_{n,n+1} = \frac{V_t - 0.5 [V_t - V_{t+1}] \frac{T_t}{T_{t+1}}}{A [(t+1) - t]}$$

$$L_{n,n+1} = \frac{V_t - V_{t+1}}{A [(t+1) - t]} - E_{n,n+1}$$

ASSUMING THAT  $S \rightarrow 0$

due to winds up to 80 miles per hour, has caused erosion requiring maintenance on about 1% of the dike edges. The present pond design may be close to an optimum for this case; however, every design must match the special conditions of an operation.

The overall solar evaluation and multiproduct processing studies are being continued to complete the process design as previously discussed. The use of solar evaporation processes in the production of numerous coproducts from multicomponent brines should be an expanding area in the future.

NOTATION

E	=	EVAPORATION RATE, IN/DAY
S	=	SALT CRYSTALLIZATION RATE, IN/DAY
L	=	LEAKAGE RATE, IN/DAY
$\Sigma$	=	SUMMATION

T	=	TRACER ppm OR WT %
V	=	BRINE VOLUME, ACRE INCHES
$\rho$	=	SPECIFIC GRAVITY
A	=	AREA OF POND, ACRES
t	=	START OF DATA PERIOD, DAYS
t + 1	=	END OF DATA PERIOD, DAYS
C	=	RATIO OF CRYSTALLIZED SALT/ EVAPORATION

#### SUBSCRIPTS

t	=	MEASURED DATA AT START
t + 1	=	MEASURED DATA AT FINISH
O	=	DATA AT TIME OF SURVEY
n	=	CALCULATED DATA AT START
n + 1	=	CALCULATED DATA AT FINISH

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