

Factors in the Design of Solar Salt Plants

Part II. Optimum Operation of Solar Ponds

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ABSTRACT

The operation of solar salt ponds is basically a simple problem, and yet like so many other evolved procedures, is subject to considerable technical improvement. A thorough knowledge of the sea water solution chemistry, both as to the phase relationships and kinetics can greatly help in solar pond control. The density limits of when iron, CaCO_3 , gypsum or anhydrite, salt, magnesium compounds, etc., crystallize are quite important to both the pond's control and productivity. In a similar manner a knowledge of the evaporation rate as a function of both the brine density and season of the year is required to anticipate the pond's most effective operation. Data is presented on both of these features of solar pond operation and control.

The general operating methods possible for the winter months, the optimum brine depth in the ponds, and the use of salt floors are discussed. Control procedures, such as brine movement and monitoring, pickle pond operation, the optimum end point of crystallization, and the need for analytical control are also reviewed along with various of the physical aspects of pond operation, such as motor equipment, pumps, weirs, and the man power requirements.

INTRODUCTION

The operation of a solar salt pond system is basically a simple combination of introducing brine into the system, allowing it to concentrate to the salt saturation point, transferring it into salt crystallization ponds, and then disposing of the bitterns prior to the deposition of excessive amounts of contaminating salts. Every company operating solar ponds has developed techniques and controls for this operation, and it is practiced with reasonable efficiency as a somewhat complex art. There is usually room for some improvement with this operation, however, especially as demands for production or salt quality increase.

The entire subject of pond operation, with special emphasis on the areas generally in need of close control, and their optimization, will be the subject of this paper.

TECHNICAL CONSIDERATIONS

Phase Relations. To thoroughly understand the operation of solar ponds it is first necessary to know the physical chemistry that occurs during brine evaporation, both in the crystallizing phase relationships, and in the kinetics, or rates of crystallization and evaporation. The generalities of sea water's evaporation path are well known, although surprisingly, the specific performance is less well defined. Usiglio (2) presents rather detailed analytical data on the evaporation of sea water, but owing to the very pronounced supersaturation occurring in his experiments, they do not too well simulate evaporation in large solar ponds. Other data (2, 5) have been obtained, however, that help to describe these phase relations.

Figure 1 shows the path of crystallization for the various constituents of sea water upon evaporation. Two of the minor components, iron and carbonate, crystallize very early in the evaporation as perhaps the iron, calcium, and magnesium carbonates. They start crystallizing immediately, and the iron is essentially removed by the time the brine reaches a density of 7° Be, and the carbonate by a density of 15. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) starts crystallizing at a density of about 13° Be (11.7 theoretically -- 7) and continues on throughout the remaining course of evaporation. However, at a density of about 16.4° Be, it should change its crystallization form to anhydrite (CaSO_4), and by a density of 27 most of it has been crystallized.

DEPOSITION OF SALTS DURING THE EVAPORATION OF SEA WATER, 25° C.

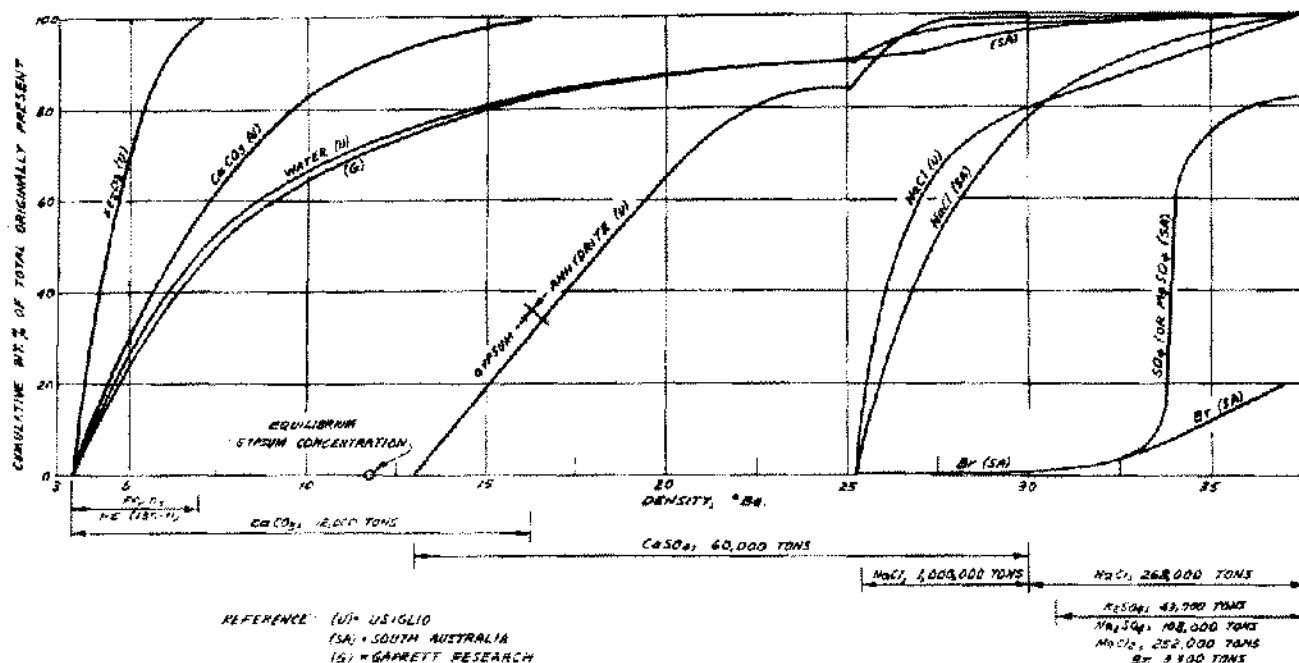


Figure 1

Salt becomes saturated at about 25.4° Be, and as with each of the remaining components, continues crystallizing throughout the course of evaporation. At a density of 29° Be, about 72% of the salt has been crystallized, and at 30° Be, about 79%. Bromine crystallizes as a solid solution of NaBr in the salt (in very small concentrations) and increases slowly in its amount crystallized as the concentration increases. As other chloride salts (KCl and MgCl_2 double salts) come down, the amount of bromine in solid solution sharply increases, but this crystallization still represents only a comparatively minor amount removed from the solution until the end of evaporation.

Various sulfate and magnesium double salts (astrakanite, etc.) theoretically do not commence crystallizing from 25° C brine until a density of 33.5° Be is reached, but owing to the evening cooling effect, the pronounced metastable concentrations that can exist, and the quite different crystallization kinetics with different salts, some magnesium and sulfate salts will appear at about 30° Be, and their concentration in the salt can be appreciable by 32 to 33° Be.

Figure 2 is a plot based upon the foregoing phase relations, showing the contaminants crystallized with the salt. The amount of gypsum or anhydrite decreases rapidly during the course of salt crystallization, although since the amount of salt depositing at the higher densities is also decreasing, the cumulative percent of CaSO_4 present decreases at a much slower rate than the instantaneous salt-to- CaSO_4 ratio. The amount of magnesium sulfate on the same scale appears to

IMPURITIES CRYSTALLIZING WITH
SALT FROM SEA WATER

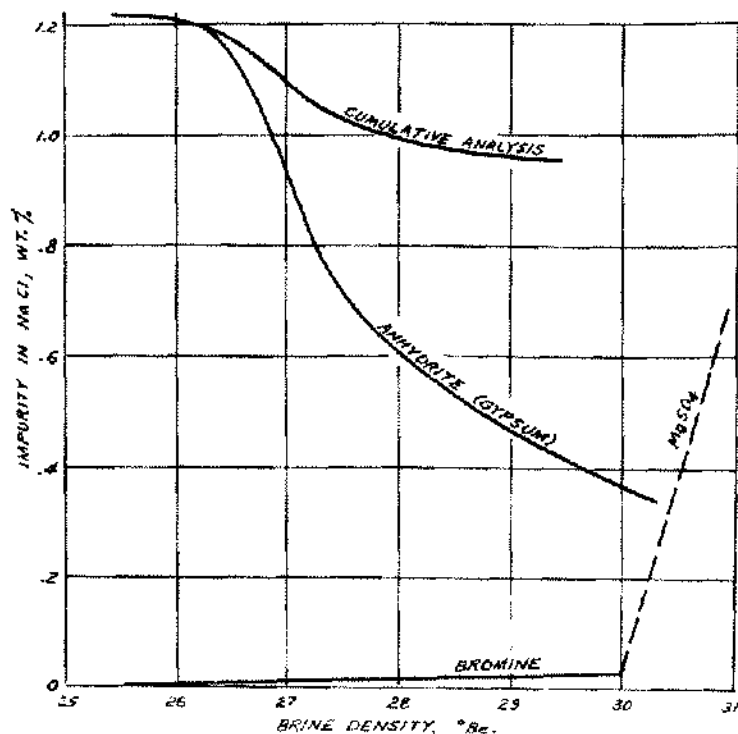


Figure 2

be large, but since it is quite soluble in water and brine, its presence should not be considered a serious impurity until much higher concentrations are reached.

As a final point of interest with sea water evaporation, the amount of water removed is also plotted in Fig. 1. This value of course varies greatly with the original sea water density, but starting with normal sea water (3.44° Be), about 92% of the water has been evaporated before salt begins to crystallize, about 5.4% of the water evaporates during the NaCl zone from 24.5° to 29° Be, and the remainder stays with the bitterns. Figure 3 shows typical concentrations of the various ions during the evaporation of sea water.

In summarizing the foregoing physical chemistry of the sea water during evaporation, several considerations are of importance. First, from a density of about 5° Be, to the salt saturation point, several phases crystallize that either can have some intrinsic value of their own, or can act as "sealants" to the solar pond floor. Since gypsum and anhydrite come down in fairly large quantities, the zone from 13 to 23° Be, is the most important in this regard. Second, it is impossible to produce a 100% pure NaCl in sea water solar ponds, since both anhydrite and bromine are unavoidable contaminants. However, their amount can be relatively small and, of course, the anhydrite may be later removed in the washing equipment. As a final conclusion, the salt yield may be considerably increased by extending the period of evaporation to 30 to 32° Be, provided that the salt washing facilities are adequate to remove the greater quantity of soluble salts, and that the evaporation rate is still reasonably high.

Evaporation Rate. The evaporation rate in the particular locale of the ponds also plays an important role in their operation. Successful sea water solar pond operations can be conducted in a wide variety of climates, but the exact operating procedures must conform to limitations imposed by the climate. Figure 4 illustrates an idealized monthly evaporation curve showing the change in rate that is normally experienced for each of the seasons. In the location shown, as is typical for many areas of the world, there is for several months a negative evaporation rate for brines of all densities (i. e., there is more rainfall than can be evaporated). Figure 5 shows

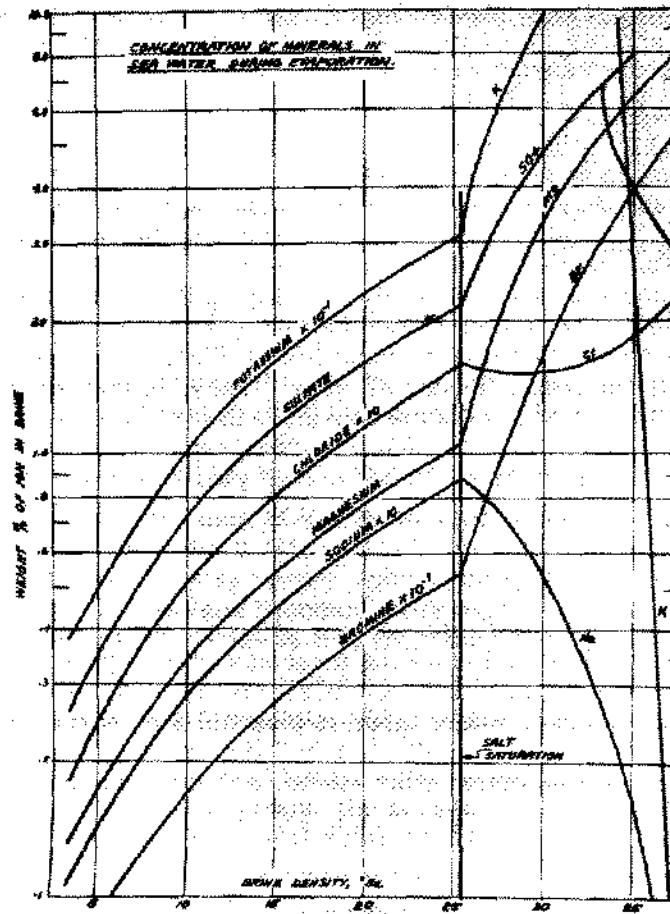


Figure 3

TYPICAL MONTHLY VARIATION OF NET SOLAR EVAPORATION RATE

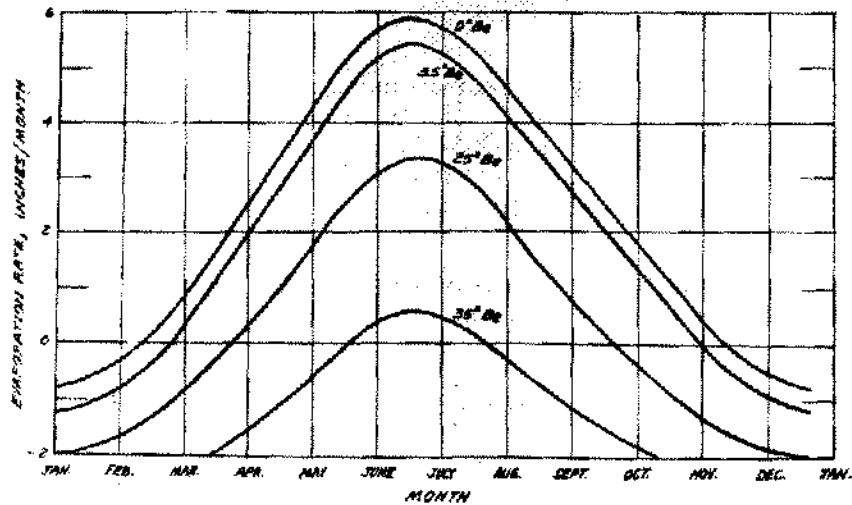


Figure 4

comparable total yearly evaporation rate data as a function of the brine density. It indicates quite clearly the wide variation of rate in different areas, and that although the initial sea water evaporation rate may be nearly that of pure water, because of the decreasing vapor pressure of the strong brines the evaporation rate of 30° Be bitterns can drop to very low values.

The methods of working within these climatic limitations vary greatly, as does the efficiency of many of the operations. In areas of extreme rainfall and short evaporating seasons, such as Formosa and East Pakistan, they shorten the evaporation cycle and work in-between the rain-storms in the border months, and throughout the dry season. By so doing, they essentially utilize the gross evaporation rate, and the production per unit area is reasonably high. Some areas, such as at Salt Lake, operate and keep the ponds full only during the dry, warm season, and work with the net evaporation rate of the dry months, again allowing a fairly high production rate per unit area. Other areas, such as at San Francisco and in New Zealand, merely accept the yearly net evaporation rate, and keep the ponds flooded all year. They, of course, produce salt only during the summer months, and their yield is commensurately lower, being based on only 15 to 30 net inches of evaporation per year. Finally, some locations, such as in Baja California, Mexico, have such a favorable climate that production can occur on a year-round basis, but at a slightly reduced rate in winter.

GENERAL OPERATING METHODS

Winter Operation. In considering the various operational cycles possible for a given solar salt plant, local conditions will often dictate the most economical procedure. However, where this is not an obvious decision, an economic optimization can be applied to help determine the best cycle. Generally it is only in areas where labor is plentiful and inexpensive that the "operate-between-storms" technique can be used. This method requires quick pumping of the strong brines into impounding basins or cisterns prior to the storm, and then draining the rain water and

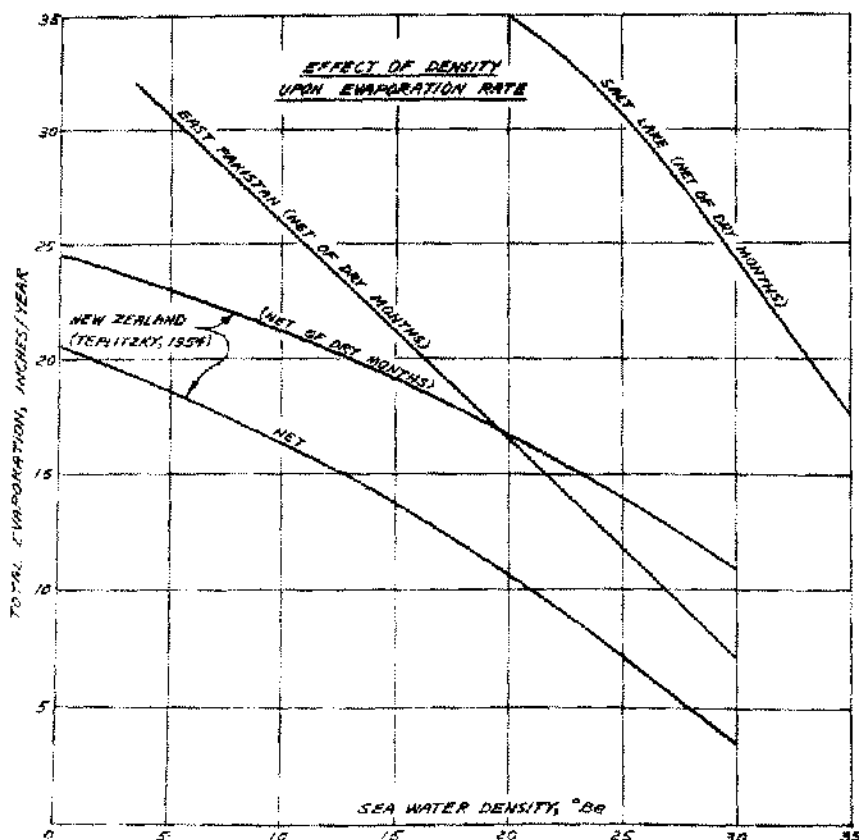


Figure 5

refilling with brine after the storm. This necessitates small pond subdivisions, many impounding basins, frequent harvesting, and considerable labor. It can be surprisingly effective even when applied to large operations (i. e., 200,000 t/yr plants in Formosa), but must be considered as a special operating case.

A modification and more generally usable form of the above method is to drain some or all of the ponds in the winter. The strongest brines should be pumped to deeper impounding basins at the end of the season for the maximum efficiency, but by careful level control this step can be eliminated or minimized. By decreasing the pond levels toward the end of the season, the amount of final brine inventory can be quite low.

An example of the potential effectiveness of this method can be seen in Fig. 5. Based upon this plot the average yearly net evaporation in New Zealand would be about 15.5 inches/year. By operating only during the summer months it could be increased to about 20.6 inches/year, or a 32% production increase. Of course, not all of this gain could be realized, and there definitely would be additional costs and operating problems. However, it does indicate that an economic analysis of the method could possibly lead to operating economies.

With a similar comparison, the data of Ver Plank (10) on the San Francisco Leslie Salt operation indicates a possible evaporation rate of 34.9"/year instead of 22.5"/year, or a 35% increase. Dike and pond bottom erosion problems, enlarged pumping capacities, and more exact pond control are all required, but as land becomes more expensive and scarce, and production demands increase, some operations should benefit from converting to this operating method.

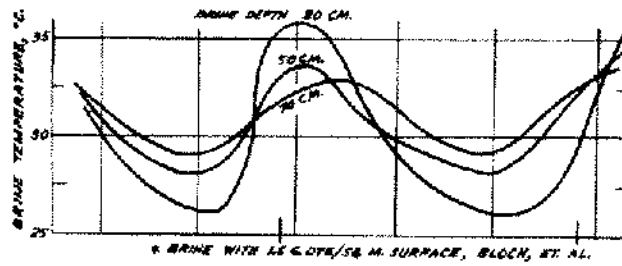
More precise data on the evaporation rate curves shown in Figs. 4 and 5 can also lead to an additional small but definite increase in salt production per unit pond area. In most areas there is an appreciable difference in evaporating rate with brines of different densities and consequently the net evaporating season can be somewhat longer with low density brines. Because of this, by the correct sequencing of brines into the ponds, the season can be lengthened. By keeping the brine depth low, the loss caused by unseasonal rains would be small, and statistically, increased production should result.

Optimum Brine Depth. Considerable study has been made of the effect of brine depth upon the net evaporation, including the excellent mathematical study by Ferguson (3). This work has strengthened the quite logical conclusion that the shallower the brine depth, the greater the evaporation rate. The reason for this is that with shallower ponds, the brine heats up quicker and hotter, and thus can have higher vapor pressures for a longer period of time. The shallow brine also gets colder in the evenings, and the deeper ponds have a more stable, uniform temperature. The net result of this is that all brines, but especially more concentrated brines (with their lower vapor pressure) respond best to shallow depth operation. However, in all cases the wind can have an overriding influence. Vigorous, uniform winds will completely nullify the effect of brine depth, and higher winds during the non-sunshine hours can even make the deeper ponds show a higher evaporation rate. Typical temperature curves for shallow and deep ponds, are shown in Fig. 6.

A possible limitation to the evaporation increase caused by the shallower depth would result from any lack of absorption of the sun's radiant energy. Figure 7 shows a smoothed curve of the solar spectrum, and the absorption of water and brine. It can be seen that the salts in the brine increase the absorption, and that a six-inch depth should account for greater than 96% retention of the solar energy, even with a perfectly reflective bottom. With silt or algae in the brine, or with a mud bottom, the absorption should be relatively complete at much shallower depths because of the absorption of the solids.

These data lead to the conclusion that concentrating ponds can be equally efficient absorbers at any depth brine, but that the crystallizing ponds should be at least four inches deep. At shallower depths the addition of a dye, or light absorber, to the brine could improve the effective evaporation rate. Several plants currently use such dyes in some of their ponds, and claim an improved salt production of from 10 to 20% (8). However, there is no commercially available additive that absorbs efficiently in the early part of the spectrum, and that can be economically justified for the general case. In special situations, however, and when inexpensive, more effective absorbers are developed, their use should find a limited but important application.

TYPICAL POND TEMPERATURES WITH VARIOUS DEPTHS OF BRINE *



* BRINE WITH 15 G DYE/SQ M. SURFACE, BLOCK, ET. AL.

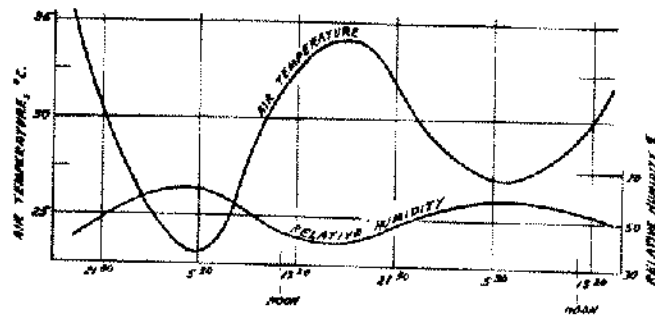
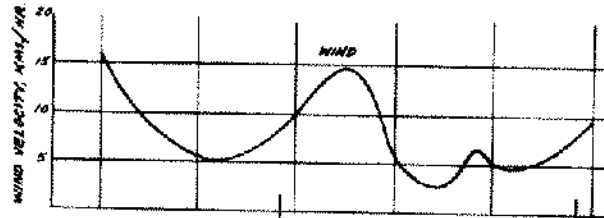


Figure 6

LIGHT ABSORPTION CHARACTERISTICS OF VARIOUS BRANES

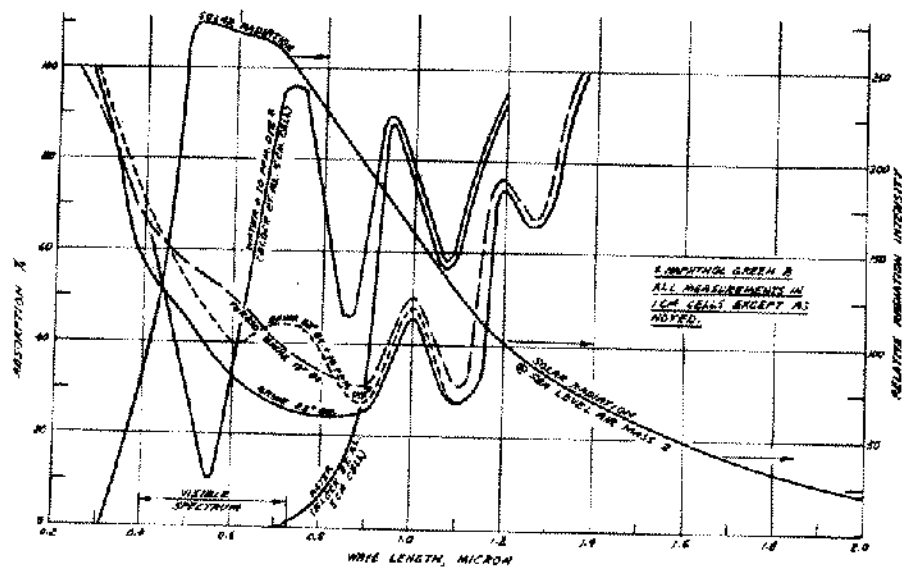


Figure 7

Salt Floors. An operating technique more related to harvesting than to pond operation, but one that dictates some of the pond control methods, is the choice of building a salt floor under the crystallizing ponds. Such a floor allows the use of less expensive and heavier harvesting equipment, and prevents mud contamination of the product salt, but does require special maintenance and protection.

The preparation of a salt floor is simply accomplished by allowing salt to crystallize in the normal manner, with perhaps an occasional rough dragging of the edges and any area of too uneven deposition. When it has reached the correct depth it should be dragged and smoothed with a scraper blade to obtain the desired slope and evenness, and all areas with depressions filled with salt. The final surface at this stage can be very rough, but it should have the desired overall flatness and contour. About one or two weeks after the brine for the first (or next) crop is flooded onto the floor, the entire floor should be dragged to strike a cleavage plane between the floor and new salt. After harvesting, the floor should be dressed and repaired again, and within a very few seasons it will be a compact, smooth, icelike mass.

The optimum depth for the salt floor will vary with the underlying clay-bearing strength and the harvesting equipment desired, but in general, six inches is a minimum, 12 inches will allow quite heavy loading, and 18 inches will support essentially any harvesting equipment desired.

The principal item of maintenance for salt floors is to prevent their being dissolved by unsaturated brine, or rain water. The former requires close control of the densities in the concentrating and pickle ponds, but this is a worth-while objective regardless of the bottom. To prevent dissolving by rain water if the ponds are to be taken out of service for the winter requires more difficult programming. Some of the crystallizing ponds can be used for winter storage reservoirs of pickle and crystallizing liquor, provided that a depth greater than about two or three feet could be maintained. For the other crystallizing ponds, the ideal shielding liquor would be bitterns, or even concentrated (i. e., 34° Be) bitterns. The ponds should be filled so that as much of the rain water as possible decants off the top of the pond as it enters, and the ponds should be refilled to the overflow level between storms. Pond bottom repair or build-up can occur on a rotational basis with salt from 30° -- 33° Be, or with 32° -- 34° Be, brine in the summer season. Such a salt floor protection procedure may not be practical if the winter storms are too severe or frequent, but the benefits of a salt floor are very substantial, and in many areas should be quite justifiable economically.

CONTROL PROCEDURES

Flow Path and Control. The methods of routing the brines, and of controlling the concentration and volumes, is basically a very simple operation. However, even with the simplicity of making density measurements and of controlling weir openings or pumping rates, many pond operations could experience a five to 15% capacity increase by more exact flow control. Several basic factors are involved: first, the more dilute the brine, the less valuable, and thus if there are pond areas of greater leakage that must be used, they should contain the weakest brine. Second, the more dilute the brine, the higher its evaporation rate, and thus the more ponds, and less back-mixing, the better. Finally, the more closely the brine is brought to the salt crystallization point, and the longer time it is held at that density, the more effective the crystallization ponds, and the less the gypsum contamination.

Free (4) has examined the influence of the number of ponds on the systems' productivity, and Myers and Bonython (6) the effect of flow changes. These studies reinforce the logic that ponds should be laid out so that the flow is fairly uniform through the pond system, and that stagnant brine pockets, or short-circuiting cannot occur. This implies that a reasonable number of pond subdivisions or internal baffles are needed, but on large systems it is still possible to have primary ponds of the size 500 to 1,000 acres without adverse effects. As the brine density increases close to the salt saturation point the pond size should decrease, since the evaporation rate reduction is greater, and the need increases for frequent movement to meet the demands of the crystallizer ponds.

In general, where a choice exists, series flow should always be used in preference to parallel flow, especially for the more concentrated brines. Also, cognizance should be taken of the

great inertia of the pond system. Considerable benefit can occur if the year's flow pattern is planned in advance on the basis of normal evaporation rate changes with time and density, and the production demand and desired harvesting schedule. Control charts can be prepared to indicate the sequence of changes needed to adapt the basic schedule to actual weather conditions and changes in production demand. In this manner the available equipment and staff can be utilized most effectively, and the operation made more a series of adjustments on a planned program rather than an "art" dictated by the day-to-day weather conditions, maintenance, labor, and production demands. Of course, there are many solar salt operations where such detailed control methods are unnecessary, but there are others where such advance planning (as perhaps set up by computer programming) can offer sizeable benefits.

In handling leakage in a pond system, as a first consideration, the weakest brines should be kept in the poorest areas. However, as a second, and longer-term consideration, it should be remembered that the deposition of iron, carbonates, and gypsum all act as effective soil sealants. It may take five to seven years for such deposition to be noticeably effective, but it does occur. This sealing action is most pronounced between brine densities of 13 and 23° Be, and thus by the periodic routing of this brine to different areas of the system, all of the ponds can be made more impervious to leakage. This is an effective sealant method and, at the present time, the only economically practical one. There are no soil sealants available, whether they be polymers (polyacrylics, flocculant types, etc.) colloids, or inorganic precipitants (lime, alum, etc.) that can be considered effective enough to warrant the price of their purchase and application.

Pickle Pond Operation. In every pond system it is necessary to have a buffer pond that accomplishes the last final amount of evaporation to bring the pond to salt saturation, and acts as a surge reservoir for filling the crystallizing ponds. The primary importance of these "pickle" ponds is obvious, but a second factor, sometimes overlooked, is the part they can play in the product salt purity. As shown in Fig. 1 gypsum and anhydrite tend to supersaturate to a great extent, and are still precipitating in large quantities just prior to the crystallization of salt. As a result, if brine enters the salt ponds undersaturated, or has rapidly reached the salt crystallization point before being sent to the crystallizers, it can deposit several times as much gypsum or anhydrite as theoretically necessary. The method of minimizing this is to operate the pickle ponds as deep (with a long residence time), and as close to saturation as possible. This allows the maximum relief of gypsum supersaturation, by depositing in the pickle pond as much of the CaSO_4 as possible.

End Point of Crystallization. From theoretical considerations the evaporation, and production of salt should continue until: (1) the evaporation rate has decreased to the point where the area in the high °Be crystallizer ponds required to yield a unit of salt is equal to the total area of concentrating, pickle, and crystallizing ponds to produce an equal unit of salt from fresh brine, or (2) the impurity level in the high °Be salt rises to the point where it exceeds the salt washing plants' capability to produce a satisfactorily pure product. In most locations the brine density for the first limitation should be beyond 34° Be, and with a well-designed plant, the second limitation should be between 32-34° Be. However, the inefficient washing and high salt loss design of most washing plants limits the density to about 30° Be, and thus results in a major operational inefficiency.

A second factor in considering the terminal brine density for the ponds is the amount of evaporation that takes place during harvesting. Since evaporation of the residual, drained brine on the salt results in contamination without commensurate salt production, it is important to consider this in the operational cycle. From the standpoint of both pond production and man power efficiency, as well as product purity, it is best to provide equipment and methods for draining the ponds completely and quickly, and harvesting rapidly. Some operators crown the salt ponds, or provide a positive slope in them for ease of draining, but in large plants the gain from this construction compared to alternative methods is seldom worth the expense, unless it occurs naturally.

The size of the salt ponds is basically a balance between this added impurity factor, and the time the pond is out of operation (or into the wet season), vs. the efficiencies resulting from larger units. With the advent of considerably improved harvesting equipment, however, detailed economic balances will now usually show that instead of the previously popular 40-to-50 acre

crystallizing ponds, 200 acres or so is a much more efficient size for large operations. This, of course, will depend upon the type of winter operation employed, and many other factors, but improved technology has definitely increased the optimum size of all the system's ponds.

Chemical Control. As part of the pond operation the actual "chemical" control requires only brief mention. The composition of sea water is essentially constant throughout the world, and unless there is fear of short-circuiting of bitterns back into the inlet suction (sometimes a very real possibility), only infrequent complete chemical analysis may be needed. Density, provided there is a careful temperature correction, affords a very good measurement of the brine's concentration up to about 29 or 30° Be. One of the few exceptions to this lack of need for other analysis would be the determination of leakage rates in individual ponds or the entire system. Here, only the precision of chemical analysis balanced against flow or volume measurements can adequately provide reliable leakage information.

MAN POWER AND EQUIPMENT

Man Power. The man power requirements for solar pond operation can vary greatly with the location and conditions, but ponds should not require many operators. A once-a-day check of densities at numerous control points, and one or several crews to move, operate, and maintain pumps and weirs, should be sufficient. One, or possibly more, crews should be engaged in dyke and road maintenance, but depending upon harvesting, operating, and plant schedules, this work could be done as fill-in or part-time work for other crews.

In general an effort must be made to balance the work load among as small a crew as possible, and this generally can be done fairly well. For instance, harvesting can be carried on for all or much of the year by normal methods in areas of mild winters, or by harvesting with a dredge from flooded ponds in areas of moderately mild winters. Alternatively, if harvesting is done on a campaign basis, other work can stop during this period to allow a shifting of man power.

Two additional factors that are of considerable importance in minimizing the cost of labor in operating the ponds are: (1) to have efficient communication equipment, such as portable radios, and/or vehicle telephones (with the great distances involved and the frequent need for quick action, constant contact among the field personnel is imperative); and (2) to have adequate vehicles and equipment for the crews. Large-tire, four-wheel drive vehicles can be most useful, and all maintenance equipment should be as mobile as possible to minimize down-time on breakdowns or emergency repairs. The majority of the maintenance should be on a planned, in-the-shop, preventive basis, but, of course, some will have to be in the field.

Pumps. In many sea water solar salt plants at least some of the brine enters through tidal gates, and thus saves the cost of pumping. In areas where the tide variation is high, and the land contours favorable, this brine can enter with enough elevation ("head") to flow through all or part of the remainder of the system by gravity. However, such locations are rare, and pumps are usually required to supplement or take the place of tidal gates. Large volume, low-lift pumps are not expensive in either first or operating cost, and have the great advantage of providing the brine when and where desired.

Theoretically the ponds should be laid out so that the brine is as concentrated as possible when pumped. This would mean that ideally the sea water is first admitted or pumped into the lowest contour section at a time when the brine is as strong as possible (most sea water in coastal areas will vary in concentration during the year because of dilution from spring rain or river dilution). It should then be pumped to the next higher contour section, and the next, etc., slowly stair-stepping uphill. Of course, in practice some compromise must be made with the most favorable time for pumping and the sea water density, and the complexity of too many pumping stations and pond subdivisions. However, the taking of tidal brine flow even when not needed or easily handled merely because it is free, or immediately lifting the brine to the highest contour elevation for later gravity flow, can result in a costly operating penalty.

The type of pumps to use is also subject to much variation. Many plants have gone to considerable expense designing "ladder" pumps, "drag" pumps, and other special designs to solve salting, plugging, shallow suction, and other problems. Although many of these devices are ingenious and work well, they are basically an expensive substitute for the inexpensive,

high-efficiency, vertical, elbow, or axial flow pumps. Both from the point of view of first cost per unit capacity, and operating cost, the savings can be from 25 to 50% for the properly selected pump. The special problems should be, and always can be solved separately. For example, the salting problem is easily solved by a very slow addition of fresh water, or periodic washing out. Similarly, adequate sumps for vertical pumps can be made on the spot, or in advance when required.

Permanent stations should be made for the concentrating pond transfer pumps, but the pond draining or filling pumps should be portable. A simple wheeled mounting, with a wash water drum attached, can be quite effective. Whenever possible, totally enclosed electric motor drives should be used, but if the transmission lines would not be economically justified, diesel engine drives should be specified. They require less maintenance and attendance than gasoline engines, and are not as subject to being salted or shorted out.

Weirs. Weir construction presents a design problem at once simple and complex. Weirs are very easy to design, locate, and use, but they can be troublesome to operate and maintain. A concrete flume and support with wooden weir boards and tightening wedges is very easily operated and low in cost, but does wear out. By using Type V, air-entrained cement the sulfate deterioration of the concrete is minimized, and the boards are, of course, expendable. By being able to knock out the wedges first, and then remove boards one by one, the operator has little trouble with salt formation. Also, salt may not form as fast, or stick as tightly, to concrete, so the flumes are fairly easily cleaned.

Alternately, wood may be used throughout, and for frequently adjusted major weirs, stainless steel (or bronze, etc.) or stainless trim may be used. Often a pond system will employ stainless weirs in the large flow-concentrating section of the ponds, and concrete or wood in the salt crystallizing section. The size and location of the weirs (or pump sections) should be moderately small and frequently spaced, but this is not too demanding a requirement, and can be balanced against the costs and operating convenience involved.

SUMMARY

The operation of solar ponds is seen to be a comparatively simple task, with at present, a fair amount of "art" involved in it. However, by taking advantage of newer equipment, and optimizing the various facets of the operation based upon fundamental meteorological and chemical data, there should be room for considerable economic improvement in most of the existing operations. Many of the factors subject to optimization have been discussed.

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