

Sea Water Desalting and Salt Manufacture

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ABSTRACT

The last fifteen years have seen marked strides in improving capacity, efficiency, and costs of recovering potable water from sea water. Desalting advancements that have a bearing on salt production are discussed, however, the most important influence of a rapidly expanding desalination capacity is in providing an alternate source of salt. Only in recent years have unit capacities of desalting plants grown large enough to make salt recovery attractive. The waste brines from such plants are far from being saturated with salt and therefore require more evaporative capacity and more steam than is normally needed for a salt evaporator. However, recovery of the evaporator condensate as distilled water will usually pay for all of the steam required. Also, the extra evaporative capacity can be of the desalination type, which is only about a third as expensive as conventional crystallizing salt evaporators. The design of such a salt evaporator will differ appreciably from conventional salt practice and will also influence, or be influenced by, the selection and design of the primary desalting plant. Cost estimates indicate that salt produced in this manner would be competitive with crude solar salt.

INTRODUCTION

The sea has been a major source of salt throughout recorded history. The only generally practical means of recovering this salt has been by solar evaporation, with the result that the water content cannot economically be recovered. The sea has also been a source of potable water for a substantial time—even 50 years ago there probably were more evaporators desalting sea water than were used by the entire chemical industry. Most of these, however, were for shipboard use; they were small and were neither efficient nor trouble-free. Only in recent years has a concerted effort been made to develop large, efficient, scale-

free, land-based desalting plants. The capacities of such plants are now in the range where it is worthwhile to consider conjunctive use for both potable water and salt production.

Much of the development work for these large desalting plants has been done under the sponsorship of the Office of Saline Water (OSW) of the U.S. Department of the Interior. While their work has covered many alternate methods of desalting, and sources other than sea water, only evaporation is now considered an economical technique for large plants working on sea water. This paper will therefore deal exclusively with evaporator developments (the desalting industry calls it "distillation," based on the old definition that covered cases where the vapor was the valuable component).

Developments under the OSW program have been mainly in the fields of improved processes and designs for large capacity plants and increasing the heat transfer performance and reducing the parasitic losses in such plants. Much of this work has little applicability to the conventional evaporated salt producer who normally starts with a saturated brine and must deal with a slurry of salt in brine in his evaporators. The desalter on the other hand need work only with what must be considered a remarkably "clean" brine, so he can use much simpler evaporators. This "clean" status has not been in existence for long. Only 15 years ago, scaling was the most serious problem, as it was in the salt industry 30-40 years ago. Today, scaling can be avoided by relatively inexpensive feed treatment and by operating within fairly well-defined temperature and concentration limits. Fouling by marine organisms was also a problem in low temperature portions of the evaporator but this can be dealt with by periodic chlorination or by thermal shocking. While corrosion is still a problem in desalting evaporators, it is no worse a problem than it is in the salt industry. It has been found

that corrosiveness can be alleviated to a marked degree by a simple but thorough deaeration of the sea water feed to the evaporator.

DESALTING EVAPORATORS

Prior to the mid 1950's, most sea water evaporators were either of the horizontal submerged tube type, for the larger capacities, or of the short tube vertical type. The short tube vertical is identical to the conventional propeller calandria salt evaporator but without the propeller. The short tubes simplified descaling, which was also a major reason for initial use of this type for salt. Scaling was alleviated but not eliminated in these early desalting evaporators by the use of additives, the primary active ingredient of which usually was a polyphosphate. The large evaporators were almost always connected in multiple effect but a great number of small vapor compression units were also built, primarily for military use.

The first real improvement in sea water evaporators was the multistage flash (MSF) system, shown in the lower half of Figure 1. This should be easily recognizable as the Alberger Process, long used for salt production. A large brine flow is recirculated through the system, being heated regeneratively to successively higher temperatures in a series of heat exchangers, the last one of which is supplied by live steam. The brine is then flashed to successively lower temperatures to supply heat to the preheaters. The preheater condensate is the product of the plant and is also flashed down through the preheaters in series. The vapor from the last flasher (or the last few flashers) is condensed by a separate flow of raw sea water, only a part of which is used as feed to the recycle brine stream. The main difference between this and the Alberger Process is that the last Alberger flasher is an open pan evaporating to the atmosphere, so no condenser is needed. The waste brine from the MSF system is seldom discarded at a concentration more than twice that of sea water, for reasons to be explained later.

The principal scale encountered in the early evaporators was calcium carbonate, which has a solubility that decreases with an increase in temperature and hence is a scale former on this basis alone. However, CaCO_3 deposition results primarily from breakdown of bicarbonate ion to CO_2 and carbonate. This is a reversible equilibrium and does not proceed far unless the CO_2 can escape, as during evaporation. Since there is no evaporation at the heating surfaces of the MSF evaporator, CO_2 loss is prevented during heat transfer and the MSF unit is much less prone to scaling than the earlier multiple effect units. Calcium carbonate scaling of the MSF heating surfaces could be kept to tolerable levels simply by use of polyphosphate additives and by operating at maximum brine temperatures no higher than about 190°F (90°C). At higher tem-

peratures, bicarbonate decomposition is much more rapid, almost all of the carbonate content is lost, and the scale deposits much more rapidly, as Mg(OH)_2 instead of CaCO_3 . The polyphosphate type additives are of essentially no value in preventing Mg(OH)_2 scaling.

The most important recent improvement in sea water scale prevention has been the adoption of the decarbonation system. This simply involves adding acid (usually sulfuric) to the sea water in an amount approximately stoichiometrically equivalent to the bicarbonate content (about 110 ppm sulfuric acid on the anhydrous basis). The acid converts all the carbonates and bicarbonates to dissolved CO_2 , which can then be stripped out of the sea water with a small flow of air or evaporator vapor. Without any carbonates or bicarbonates left, there can be no shift in pH of the sea water as it is heated or evaporated and scaling by CaCO_3 and Mg(OH)_2 can be eliminated completely.

This decarbonation method of feed pretreatment helped the MSF process primarily by permitting use of much higher operating temperatures, which made it possible to save on heating surface requirements and to build less expensive and more compact plants. It also made practical the use of large capacity multiple effect evaporators, which formerly were more prone to scaling than the MSF system. The multiple effect flowsheet normally used for sea water is shown in the top half of Figure 1. The evaporator is operated forward feed, so that only low sea water concentrations are encountered at the higher temperatures. Sea water feed is taken as a small sidestream from the condenser water circuit and is treated by decarbonation and deaeration. It is then passed through a regenerative feed heating circuit much as in the MSF plant before feeding to the evaporating tubes of the first effect. From here on, both the evolved vapor and the residual brine pass to the succeeding effects of the evaporator in sequence, with the brine from the last effect being discharged at about 10.5% total solids.

Although only five effects are shown in Figure 1, an actual sea water evaporator will usually have about a dozen effects, giving a steam economy on the order of ten pounds (4.9 kg) of evaporation per pound (0.49 kg) of steam used in the first effect. This is about three times the number of effects usually used in a salt evaporator and is a result primarily of the lower cost of the sea water evaporator per unit of capacity. An important additional influence is the low capital return rate normally expected for these plants, which usually are government owned. The relationship between steam economy and number of stages in a MSF plant is somewhat different and these plants usually need on the order of 35 to 40 stages to give a steam economy of ten.

Since scaling problems are negligible, the type of evaporator used in sea water service is determined primar-

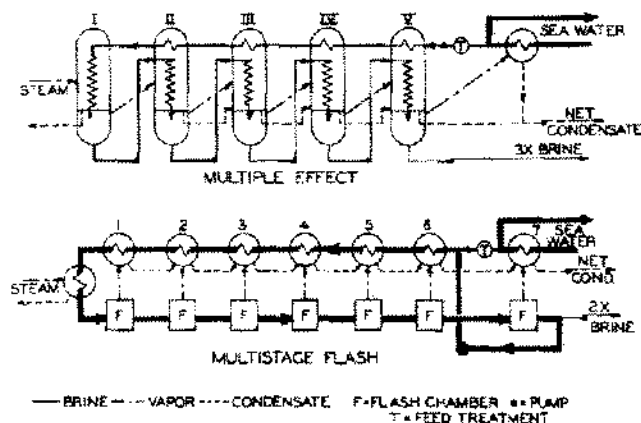


Figure 1. Normal seawater evaporator flowsheets.

ily by cost per unit of capacity. The type currently favored is the falling film evaporator as indicated schematically in Figure 1. Here, the brine flows as a film down the inside walls of fairly long, large diameter tubes. Heat transfer is directly across the tube wall from condensing vapor to boiling brine and parasitic losses in temperature difference due to pressure drop, etc., are usually negligible. Other types that have received appreciable attention are the LTV, where the brine boils as it flows up the tubes, and the horizontal tube, or "spray film" evaporator. The first of these is widely used in industry in non-salting service and the latter is similar to the old Lillie; brine is showered over horizontal tubes rather than the tubes being immersed in brine. None of these evaporator types is new—for instance, a triple effect Lillie was working on sea water in 1900 and an octuple effect in 1916.

Much work has been done under OSW sponsorship on improving heat transfer in these and in the MSF evaporator. Attempts have been made to develop a practical means of promoting dropwise condensation. The only essentially permanent method, however, is gold plating, which costs more than it is worth in terms of improved performance. For the MSF evaporator, the most promising heat transfer improvement has been the "roped" tube, which has spiral indentations rolled into the wall. This gives a marked increase in heat transfer coefficient, although at the cost of a substantial increase in pressure drop and hence in power consumption. The primary uncertainty with these tubes is with regard to their sensitivity to accelerated erosion. They certainly would not last long in crystallizing service, as in a salt evaporator.

Most of the heat transfer improvements for the multiple effect evaporator have been for the falling film version. The roped tube shows much better heat transfer performance than the smooth tube in this service also, and the increased pressure drop is much less of a penalty than it is when used in a MSF evaporator. Another enhanced

heat transfer surface involves use of a sintered porous metal surface on the boiling side that provides an abundance of nucleation sites for improved boiling heat transfer. The disadvantages here are cost of the tubing and the overconcentration of brine in the pores of the coating, which increases the risk of scaling. The most thoroughly developed enhanced surface for the falling film evaporator is the doubly fluted tube, which gives close to three times the heat transfer coefficient of a smooth tube. This tube has longitudinal flutes rolled into the surface on about a 1/8" (4 mm) spacing. Enhancement on the steam side results from surface tension forces that draw condensate into the grooves and leave the lands with only a very thin film of condensate that has little resistance to heat transfer. Enhancement on the boiling side is also substantial, for reasons that as yet are not fully understood. Although these tubes are appreciably more expensive than smooth tubes, they still give a substantial net gain in performance per dollar of installed surface cost, at least where fouling resistances are low, as they are in a sea water evaporator.

The same doubly fluted tubes also yield improved heat transfer performance in the conventional upflow LTV evaporator. Here, the gain is mainly on the steam side, the gain on the boiling side resulting primarily from the increased surface area that results from fluting (about 28%). An important finding for this type of evaporator is that the addition of even small amounts of surfactant can yield a marked improvement in heat transfer. Even the traces of surface active agents present in normal sea water result in higher heat transfer coefficients being obtained on sea water than on pure distilled water.

It can be seen that the types of evaporators used for desalting and the improvements in their heating surfaces are applicable almost exclusively to clear solutions and are of little help for crystallizing service as is needed in the salt industry.

DESALTING PLANTS AS A SOURCE OF SALT

Although desalting plant developments do not provide much direct help to the conventional salt producer, they do point the way to practical plants for combined production of potable water and salt. Figure 2 is a diagram showing the operating ranges that must be covered to make salt from sea water. The upper hatched area shows the proportion of the total evaporation required after the point has been reached where the brine is saturated with salt. Since salt production per unit of evaporation is practically the same for concentrated sea water as for saturated wet-mined brine, the hatched section corresponds to the total evaporation required in a conventional salt plant. The remaining area represents the extra evaporation that must be accomplished when working with sea water.

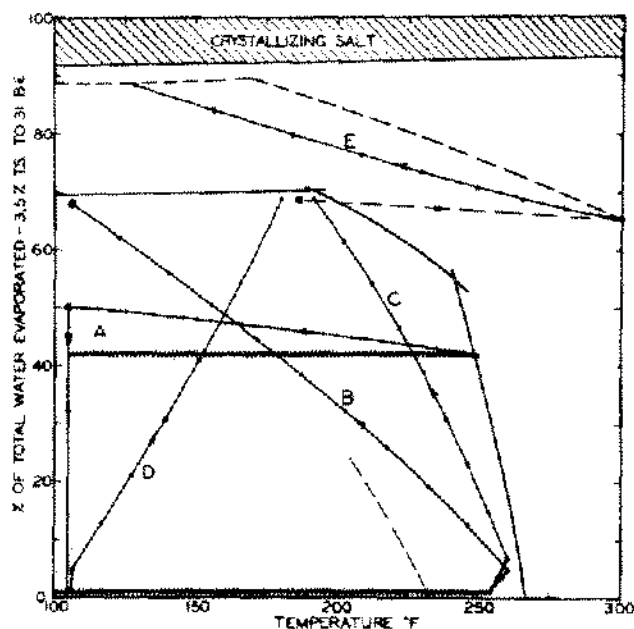


Figure 2. Seawater concentration diagram.

The normal operating range for desalting plants is that area inside the shaded boundary on the lower left hand side of Figure 2. This area corresponds to operating conditions where CaSO_4 deposition does not occur. At low temperatures, gypsum solubility limits maximum water recovery to about 70% of the total that must be removed to make salt. At higher temperatures, recovery is limited by the solubility of $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$. At still higher temperatures, anhydrite scale formation provides the limit. This latter curve is not a true solubility limit, but a curve representing a degree of supersaturation that usually can be tolerated without scale formation in a sea water evaporator. The curve actually corresponds to a scale growth rate of about $1/8''$ (4 mm) per year on a tube initially scaled with CaSO_4 .

Curves A in Figure 2 represent the normal operating conditions in a MSF plant, where there is not a large increase in concentration in one pass through the system. The sea water makeup rate is usually regulated to maintain about 50% overall water recovery, which is a compromise between cost of feed pretreatment and the desire to operate at the maximum top brine temperature in order to conserve on heating surface needs. Operating conditions for the usual multiple effect plant are shown by curve B. Low concentrations at the high temperature end permit use of the highest possible top brine temperature and only gypsum solubility at the low temperature end limits maximum water recovery. The discharge concentration from this evaporator is controlled in practice simply by adjustment of the ratio of steam to sea water feed rate.

An additional advantage of a multiple effect evaporator for this service is that other feed combinations are also

possible, such as backward feed, or parallel feed as is usually used on salt. A good feed sequence for a desalting evaporator when salt recovery is also desired involves combined backward and forward feed operation. By reducing the ratio of feed to steam of the previous forward feed system, brine concentrations will increase faster, as in Curve C. Brine at maximum practical concentration is then withdrawn from an intermediate effect and the vapor from this effect heats another section that is operated backward feed, along path D. Two brine streams are thus available at high concentration and high temperature for further processing. This method of operation is not as efficient as the normal forward feed sequence, requiring one or two extra effects to achieve the same steam economy. However, there are other advantages that make the total cost for the desalting plant operator equal to or lower than that of the conventional arrangement. These advantages result from the fact that discharge of the brine hot reduces the evaporation rates and heat loads at the low temperature end of the plant. This reduces loads where heat transfer performance is poorest and entrainment separation requires the most vessel volume. It also results in a marked reduction in sea water volume required simply to cool the final condenser, and hence in intake system requirements.

There are a number of possible ways for bridging the gap between the brine concentration that can be produced economically by the desalting plant operator and the saturated brine desired by a salt producer. One would be by use of a forced circulation evaporator seeded with CaSO_4 , but this type is about three times as expensive as a desalting evaporator per unit of output. Considerable success has also been encountered with seeded falling film evaporators in this service, but the work has been primarily at constant temperature conditions, as in a thermocompression evaporator. Another way is to preheat to such a high temperature that the solubility of anhydrite is greatly reduced and the rate of crystallization of anhydrite is reasonably high. Since preheating involves crossing a region where scaling would be expected, the preheating would most safely be accomplished by direct contact with steam. This will dilute the brine somewhat, as shown by the dashed line in Figure 2. If the brine is preheated to 300°F (149°C) and brought to equilibrium with anhydrite, about 85% of the original CaSO_4 content will precipitate and this will raise the region in which scaling can be avoided to the upper shaded lines in Figure 2. Thus this brine could be concentrated in a conventional forward feed desalting evaporator along curve E almost all the way to saturation with salt before re-encountering the gypsum solubility limit. The short remaining distance to the salt saturation curve could be handled by a single gypsum seeded, forced circulation effect on the end of the concentrating evaporator, or in the salt evaporator itself.

The reason for wanting to preheat the concentrated

brine from the desalting plant to a fairly high temperature is shown by the crystallization rate data of Figure 3. The value plotted is the rate constant in the equation:

$$-dC_{Ca}/d\theta = k_s A (C_{Ca} \cdot C_{SO_4} - K_{sp})$$

where
 C_{Ca} , C_{SO_4} are concentrations in moles per liter
 θ , is time in minutes
 A , is crystal surface area in cm^2/liter of solution
 K_{sp} is the solubility product of anhydrite in $(\text{moles/liter})^2$

The Japanese data (Moriyama and Utsunomiya, 1957) were originally plotted as a straight line on these coordinates but our own data on sea water at 300°F (149°C) indicate that the line is actually curved. The actual crystallization rate at 300°F is over 20 times faster than originally thought, which makes possible the use of a relatively small seed contactor for this duty. There is no magic in the 300°F temperature—the actual temperature would usually be dictated by available steam pressure. However, the highest practical temperature is desirable, both to precipitate the anhydrite as rapidly as possible and to precipitate as much as possible.

A flowsheet for such a unit is shown in Figure 4. The

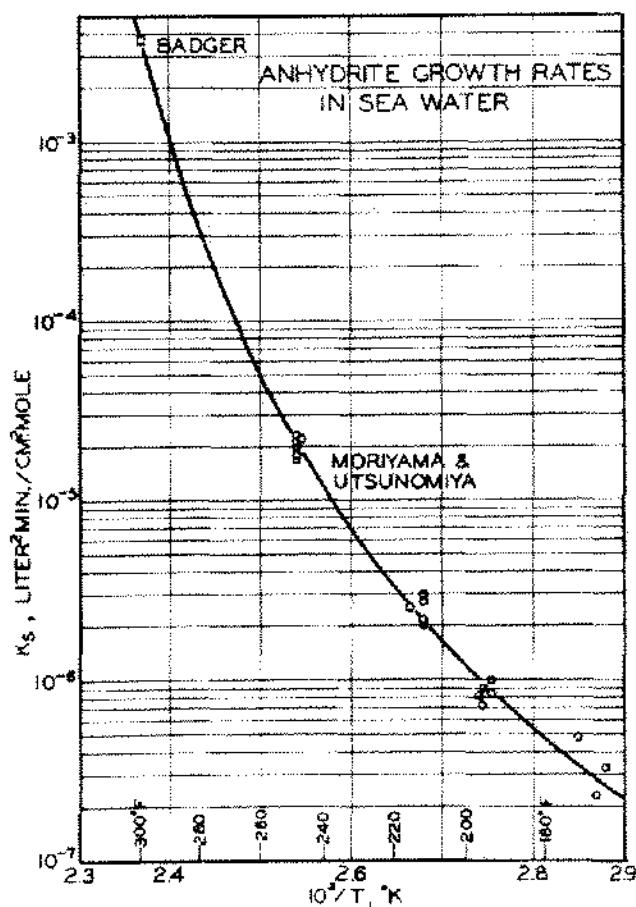


Figure 3. Anhydrite growth rates in sea water.

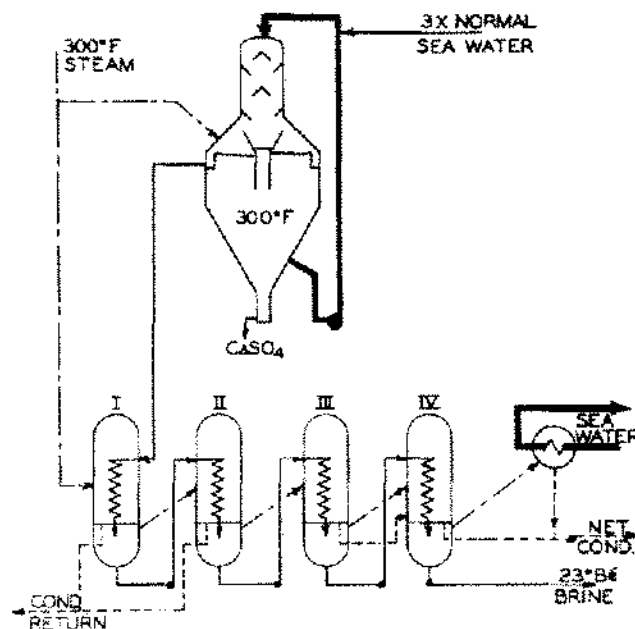


Figure 4. Brine concentrating evaporator.

direct contact heater, the seed contactor, and a clarifier section to hold back the anhydrite seeds can all be built into a single vessel. The direct contact heater would be similar to a barometric condenser, mounted in the top of the vessel. A fairly thick seed slurry would be circulated through the condenser with the feed in order to avoid scale buildup on the condenser baffles. The excess CaSO_4 would be discharged through an elutriation leg, which is provided primarily to permit quenching the slurry with a small feed of cool brine. The evaporator following this contact vessel would be a conventional sea water desalting evaporator but would not need the feed preheaters that are a part of the normal evaporator. Part of the water evaporated from the brine in this unit would have to be returned to the power plant as makeup for that portion of the steam used for direct contact heating, but overall production of potable water would be the same in any case. The principle advantage of this arrangement is that evaporation can be accomplished in an inexpensive desalting-type evaporator at a total cost, per unit of distilled water recovered, about the same as that when handling normal sea water. Thus the incremental cost of producing an almost saturated brine in this manner would be very low.

After the brine has been brought close to saturation with respect to salt by this or an alternate system, it can be (and has been) handled in the same manner as in a conventional salt evaporator. The only difference is that the content of soluble impurities (mainly MgCl_2 and MgSO_4) is higher than normally encountered, requiring a higher purge rate and closer attention to recovery of heat and salt from the purge.

ECONOMICS OF SALT PRODUCTION

Two rules-of-thumb are helpful. One is that the yield of salt from a combined plant would be about 100 tons of salt per million gallons of total potable water produced. The other is that total operating cost will be about 20% higher to go all the way to salt than to operate a plant to produce only potable water. The latter includes capital charges in the operating costs and assumes that both water and salt production are under one management. Since desalting plants are now being built in the 2 to 10 MGD (8,500–40,000 m³/d) range, salt yields would be in the range normally encountered by salt producers. A five MGD water plant could be made to yield 500 tons per day (TPD) of salt and a water plant this size would normally have production costs on the order of \$1.00 per thousand gallons (\$0.265/m³), if only water is produced. At a 20% higher cost when producing salt, the total cost would be \$1.20 per thousand gallons if all were charged to the water, or \$2.00 per ton of salt if water were credited at the cost from a water-only plant.

However, it probably would be more likely that a different situation would prevail, wherein the water plant was owned by a public utility and the waste brine was delivered over the fence to a salt producer. The utility probably would expect a lower return on investment than would the salt producer, resulting in a lower water credit for the distilled water returned by the salt producer. Nevertheless, if steam and power were purchased from, and the distilled water resold to, the utility at the utility's costs of production, the income from the sale of distilled water made by the salt producer would just about pay for his requirements for steam and power. The principle salt production costs would therefore only be for labor and equipment amortization. Under these conditions, the salt cost would be higher than given by the 20% rule-of-thumb, but still reasonable. A detailed estimate of costs on this basis was recently made for a projected plant in Puerto Rico (Burns and Roe, Inc. and Dow Chemical Co., 1971). The results are shown in Figure 5. For this case, water production cost from the main plant was 45¢ per thousand gallons and the projected cost of an alternative supply of solar salt was \$4.18 per ton. Thus for these conditions, the discounted cash flow for the salt producer was 17.5%, which should be quite attractive. Admittedly, this study was for a fairly large plant (one million tons per year), with a captive salt market. For a smaller plant, production costs would be higher, but the value of the distilled water would also be substantially higher.

An advantage for evaporated salt production in this manner would be that the supply would be steadier and the purity higher and more uniform than that of solar salt. No credit was taken for this in the Puerto Rican study and no allowances were made for costs of storage and reclaiming of solar salt from storage, or for weathering losses in

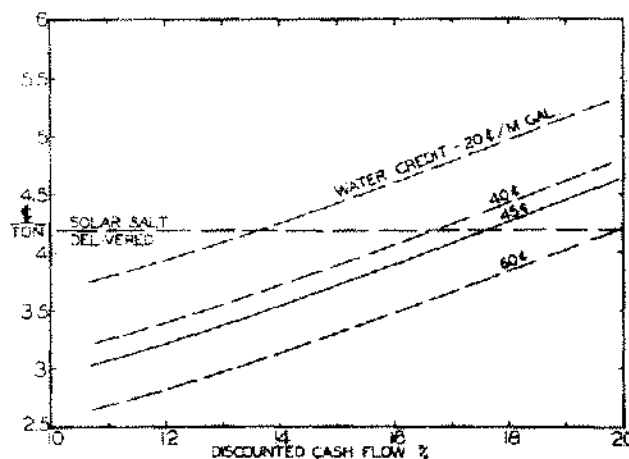


Figure 5. 3000 TPD salt plant return.

storage. The principle disadvantage for an evaporated salt plant would be when the salt was to be shipped elsewhere. Since the salt would be similar in purity and grain to normal vacuum pan salt, it would be more difficult to handle and unload than coarse solar salt.

MISCELLANEOUS

One factor demonstrated in the sea water program was that deaeration could be of substantial benefit in reducing corrosion. Figure 6 shows how this might be applied to a conventional salt evaporator. The main stream requiring deaeration is the raw brine feed. This stream generally is cold and could be deaerated effectively by last effect va-

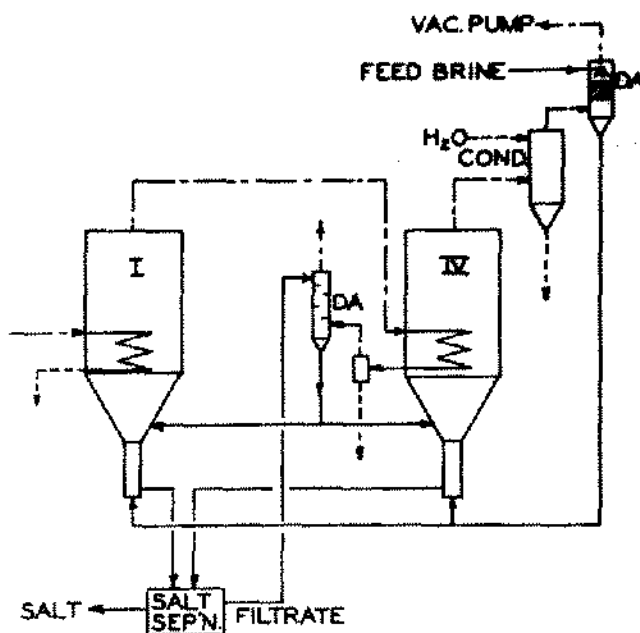


Figure 6. Deaerators for a vacuum salt plant.

pors. Placing the deaerator in series with or atop the final condenser would have the advantage of stripping most of the vapor out of the non-condensable gases, greatly easing load on the ejector system. In this position, the deaerator would heat the brine almost to the last effect temperature and the heating and dilution would make the brine unsaturated in both NaCl and CaSO_4 , which should make it easier to handle (and also could be used as a means of redissolving scrap salt at no recrystallization cost). Surprisingly enough, this heating of the brine by direct contact with waste vapor actually would save about 6% in overall steam consumption of the evaporator, justifying the deaerator on this basis alone.

The other stream that could be rendered less corrosive by deaeration is the filtrate from the filters or centrifuges used for salt recovery. This stream is somewhat hotter than last effect brine, so the best source of stripping vapor probably would be next-to-last effect vapor. If this vapor were taken as vents from the last effect, it should yield a noticeable improvement in last effect performance, due to the reduction in non-condensable gas concentrations. Since deaeration in this position uses vapor that otherwise could accomplish some additional evaporation in the last effect, the gain in overall steam economy of the system is lower—only about 2%. However, the heating and dilution in a deaerator here should be enough to dissolve up to 4 or 5% fines, which are normally present in the filtrate. Thus the main secondary benefit of this deaerator would be a reduction in trouble with level control valves, etc., and elimination of excess fine salt that sometimes can make crystal size control difficult.

CONCLUSION

In the past, most desalting plants were small and were located in very arid regions where salt could be produced quite inexpensively by solar evaporation. The present trend is toward larger plants located in some cases where solar salt production is impractical and appreciable salt markets exist. Serious attention should therefore be given to combining salt and distilled water production from sea water. Planning for such plants should start before the desalting plant is built, in order to secure a type of desalting plant best suitable for combined production.

Going back to the 20% rule-of-thumb, a desalting plant that could produce 2 to 5 MGD of water at \$1.00 a thousand gallons could produce water and 200 to 500 TPD of salt at 20% higher cost. If all costs were charged to salt production, the salt cost would be \$12.00 per ton. This is quite acceptable in some areas of the world, especially since the salt product is a table grade vacuum pan salt. Thus there is the possibility that such plants will be built for salt only, with the distilled water being discarded if no market is available.

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