

Optimisation of Production and Quality of Solar Salt from New and Existing Solar Saltfields using Brine Mass Balance Computer Modelling.

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ABSTRACT.

The authors have extensive experience in the design, construction and operation of large solar saltfields; principally in Western Australia. They now act as independent consultants advising clients on the design of new saltfields and in achieving optimal production and quality of salt from new or existing solar salt operations.

New computer-based modelling programmes have been developed which firstly assist with optimising initial solar saltfield layouts in new locations; and secondly assist with the tasks of optimising production and quality of salt from both new and existing solar saltfields.

The financial benefits accruing from these programmes include reduction in capital costs in establishing the fields, and in the reduction of operating costs throughout the life of the fields.

The association with Salt Partners Ltd. brings complementary expertise towards the achievement of these optimisation objectives.

The programmes are flexible enough to deal with all of the major variables unique for each location. These include seawater or brine input density, climatic conditions, seepage rates and production quality requirements.

A critical input into the programmes is the knowledge the authors bring regarding the evaporation rates of brines at varying densities, correlated with standard freshwater evaporation rates in evaporimeters, and the way in which these rates change from month to month. This input is a key requirement for both the initial design phase and layout of the field, and for the subsequent optimisation of production and quality of salt from the field.

High construction and operational costs at the Western Australian solar saltfields, together with the demands of the emerging chloralkali industries of Asia for high quality salt, drove the production and quality optimisation objectives of these producers.

As the programmes enable operational staff to closely monitor brine flow throughout the field, both chemical and biological control is achieved. This ensures that the quality of salt deposited in the crystalliser ponds is predictable in both series and parallel flow systems. Washing plants can therefore be designed to minimise capital and operating costs for the production of high quality salt.

These objectives are now being embraced by solar salt producers throughout the world. Additional areas suitable for large-scale solar saltfields are becoming difficult to locate. Environmental issues also limit the availability of new areas; particularly in the high productivity-per-hectare locations such as Australia and Mexico.

The lack of surplus solar salt worldwide has forced China to revert to vacuum salt utilising underground rock salt deposits. China may have installed up to an additional 10 million tonnes of vacuum salt capacity in 2007. This process is extremely energy-intensive compared to the free use of solar energy in the production of solar salt. However, the new chemical plants in China are now being serviced with high vacuum quality salt, albeit an expensive alternative to high quality solar salt using free solar energy.

The majority of this increased demand for salt in China is from the growing alkali industries in that country. As the ion exchange membrane process is now the principal technology employed by new chloralkali plants, access to high quality solar or vacuum salt is essential. This represents an

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opportunity for Indian salt exporters to supply salt at higher prices provided that the quality is similar to vacuum salt or Australian solar salt.

The authors, therefore, in association with Salt Partners Ltd. are well placed to advise the Indian solar salt producers in meeting the increasing demands of domestic and export markets for competitively priced high quality solar salt. This quality is acceptable to both chemical and edible salt markets.

INTRODUCTION

The basic operation of a solar saltfield incorporates the progressive concentration of seawater in a series of large open ponds, called concentration ponds; followed by further concentration of the brine, now saturated in regard to sodium chloride, in a further series of ponds called crystalliser ponds. Sodium chloride salt precipitates out in these ponds.

The crystallised salt is harvested from the crystalliser ponds and is usually upgraded by various washing processes which ensure the final product meets customer specifications.

Global demand for salt currently exceeds 230 million tonnes. Around 40 percent of salt production is by the solar evaporation of seawater. Until the 1960s, China and India dominated the production of solar salt worldwide, and they still remain major producers.

Historically, productivity and quality of solar salt produced in China and India was low. As alternative supplies were unavailable, customers using this salt for both edible and chemical production purposes accepted this quality.

The rapid growth of the Japanese chloralkali industry during the 1960s and 70s, using new high cost technologies, drove the demand for higher quality, competitively priced salt. This demand could not be met from Japanese domestic supplies. New solar salt production facilities were therefore constructed in Mexico and Australia to meet this demand for high quality salt. These new producers were all supported by Japanese companies.

The Mexican and Australian producers continue to dominate the supply of salt to Japan. They have continually increased production to meet demand from new chemical customers in South Korea, Taiwan and Indonesia. Again, these countries were incapable of supplying their own salt, either from solar saltfields or from rock salt deposits.

Whilst prior to the advent of the solar saltfields in Mexico and Australia, solar salt from China and India was exported in limited quantities to Japan and other Asian countries, such exports now only occur during brief periods when supply from Australia or Mexico are disrupted due to adverse weather conditions.

In the mature salt markets of the US and Europe, high-quality salt dominates the edible salt markets. However, the majority of this salt is produced from rock salt deposits using the energy-intensive vacuum process. Chemical plants in these countries also utilise these rock salt deposits. Where feasible, these plants are located adjacent to the salt resource. This enables them to directly utilise the saturated brine produced by the injection of freshwater into the salt deposit; thus eliminating the energy-intensive crystallisation process. However, the brine still undergoes a purification process prior to its use in the new generation of ion-exchange chloralkali membrane plants.

Unlike most chemical processes that take place in contained plant and equipment, the production of solar salt must accommodate several uncontrollable external factors, such as variations in climatic conditions and brine lost through seepage. Over time, diligent collation of actual climatic and geotechnical conditions at operational saltfields enables the more effective design of new fields in the general area and more efficient operations at existing fields.

To ensure the recovery of salt meets the objectives of both quantity and quality, precise control over the movement of large volumes of brine through the ponds must be maintained at all times. This control is achieved primarily through the use of a continuous Brine Mass Balance over the saltfield.

New computer-based Brine Mass Balance Models have now been developed which incorporate public domain methodologies for the design and operation of large solar saltfields, plus essential unpublished

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data which utilises know-how acquired by the authors during their long involvement in the solar salt industry.

For a greenfield operation, an preliminary brine mass balance model is developed using the best available freshwater evaporation rates, rainfall amounts, seawater density, and anticipated seepage losses from the area under consideration. This provides an estimate of the average annual production which could be expected from the available area.

Alternatively, if several sites are under consideration, the design will determine which site will best achieve a target average production rate.

Further optimisation steps may be made incorporating economic and operational criteria. The number and orientation of concentration ponds will be optimised so as to reduce the initial capital costs for construction of pond levees, pumping stations, transfer weirs etc., whilst at the same time ensuring that the final layout will not compromise the efficient operational control of brine hydraulics, chemistry and biology.

The number and layout of the crystalliser ponds will also be optimised as consideration is given to topographical conditions, harvest timing, pond downtimes, seasonal variations etc.

Following the preliminary design phase, based upon the anticipated average annual conditions, a more sophisticated model has been developed which incorporates forecast average monthly conditions.

As is well known by saltfield operators, there are significant annual, monthly and daily variations in some of the variables, particularly insofar as evaporation rates and rainfall are concerned. To optimise productivity, therefore, operators need to effectively respond to these rapid changes in conditions.

To study the magnitude of the effect of the monthly variations on brine flow rates throughout the field, therefore, the mass balance is now calculated for each month. These monthly mass balances are used to provide estimates of the range of seawater intake volumes and bitterns discharge flow rates. The determination of final design flow rates will require the development of a dynamic brine mass balance model with a control scheme imposed upon it. This model will become the tool for studying the response to upset conditions and ultimately will be used for operational control on an ongoing basis.

The objective is to recover for sale around 90 percent of the sodium chloride precipitated in the crystalliser ponds as the brine concentrates from the maiden brine density of around 1.216 mg./ml. and the normally targeted exit bitterns density of 1.25gm./ml. The 10 percent losses occur during harvesting, transportation, washing, stockpiling and recovery of the salt prior to shipment.

A number of new techniques are now available, firstly to decrease these losses, and secondly to increase the recovery of sodium chloride through more effective use of the residual bitterns brine which, at a density of 1.25 gm./ml., still contains up to 25 percent of the incoming sodium chloride in the maiden brine.

The target final product specification, as typically demanded by customers operating ion-exchange membrane chloralkali plants, is shown in Table 1:

Planned Specification of Project Product SPT			
Component	Range		Average
	% w/w basis		
	High	Low	
Sodium Chloride	97.794%	97.286%	97.540%
Moisture	2.526%	2.000%	2.284%
Calcium	0.026%	0.042%	0.034%
Magnesium	0.042%	0.026%	0.018%
Sulphate	0.125%	0.083%	0.104%
Potassium	0.020%	0.010%	0.013%
Insolubles	0.009%	0.005%	0.007%

Table 1: Assumed Final Product Specification for Solar Salt

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BRINE MASS BALANCE MODELS – METHODOLOGY

It is not intended in this paper to discuss comparative theoretical methods for designing solar saltfields. The Bibliography at the end of the paper contains a representative list of published papers for those who wish to gain a basic understanding of the theory of the production of salt by solar evaporation of seawater.

The methodology used by the authors to establish a computer-based brine mass balance model for the basic design of a new solar saltfield is now discussed.

Based upon the available area, an estimate is established of the target average annual production tonnage to be achieved from the operation; assuming the final product specification is as indicated in Table 1.

The four major solar salt producing regions of the world are:

- The northwest of Western Australia
- The Gujarat State of India
- The Bohai Bay of China
- The Baja area of Western Mexico

Much is known of the evaporation and rainfall rates in each of these regions. Approximate annual production rates from many of the larger fields in these areas are also well known. This information is used to estimate either the area required for a target production rate, or the production rate likely to be achieved from a specific area. This first order estimate is utilised in the first run of the computer model.

Based upon the target product specification, the actual quantity of solid sodium chloride (NaCl) which will be contained in the annual production is determined.

Assuming the product specification in Table 1, a production volume of one million tonnes will contain, on average, 975,400 tonnes of NaCl.

Estimate the most probable level of losses of solid NaCl salt from each of the processing steps after crystallisation of the salt in the crystalliser ponds.

Assuming a final production rate of one million tonnes, Table 2 is an example of losses of NaCl expected at each of the processing steps following the harvesting of the salt from the crystalliser ponds. This assumes that the salt will be washed in a standard washplant similar to those currently used at Australian and Mexican operations. Recent advances in washing technology and in the recovery of some of the salt lost during the washing process further reduce the overall losses of NaCl.

In this example, therefore, the amount of NaCl required to be deposited in the crystallisers, given average evaporation, rainfall and seepage losses, is 1,091,812 tonnes.

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NaCl passing through each activity accounting for losses.		
Activity	Factor to account for losses	NaCl passing through
	%	tonnes
As shipped		975,400
As crystallized		1,091,812
After harvesting	1.0%	1,080,894
After wet salt haul	0.5%	1,075,490
After washing	7.0%	1,000,206
After stockpiling	1.0%	990,204
After recovery and barging	1.0%	980,302
After transfer to ship	0.5%	975,400
Product shipped	1,000,000	SPT
NaCl content	97.54%	

Table 2: Estimated Losses of NaCl from Crystallisers to Final Product

Using the best available local data, establish forecasts for annual and monthly rates for rainfall and freshwater evaporation, from an International Class A evaporimeter.

Whilst the first order design only requires the average annual evaporation and rainfall rates, monthly rates, if available, will improve the accuracy of the program. Table 3 provides indicative monthly evaporation and rainfall rates for North West Australia and the Gujarat region of India.

Across the area covering the location of the five fields in the North West region of Western Australia, annual evaporation and rainfall averages taken over many years are reasonably close. However, rainfall associated with cyclonic activity varies greatly and may only effect one saltfield. Similarly, rainfall during the winter season may also be significantly different from one field to another. Hence the need for the operational brine mass balance programs to be flexible enough respond effectively should such events occur. In India the monsoon season also imposes unpredictable rainfall events to specific saltfields. It is noted that whilst negative evaporation months, those when rainfall exceeds evaporation, occur infrequently in Australia, such may not be the case in India. It is standard practice in Australia to shut down all brine movements following high rainfall events; allowing the field to return to normal over time. It is understood that various practices are employed at saltfields in India in response to these periods of negative net evaporation. The models will need to be adjusted to include accepted practices at each saltfield.

Establish most probable average density of incoming seawater to the concentration ponds, and confirm level of major elements in this brine.

In the absence of specific data, the principal source of NaCl is assumed to be that found in normal seawater. As defined by Baseggio, seawater from open oceans usually has a density of around 1.0247 SG at 22.2°C. However, many large solar saltfields do not have access to constant supplies of such normal seawater. In Australia and Mexico, some saltfields have access to a constant supply of seater which has been pre-concentrated by as much as 14 percent due to large creek or lagoonal areas. The configuration of the Australian and Mexican salt fields negate dilution of the seawater by run-off from rainfall or river systems in the general area. Such is not the case in areas of China and India where significant dilution may occur during periods of each year.

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Thus, although the initial design may be based upon the estimated annual average of seawater density, the brine mass balance program can run options to estimate the effect of both pre-concentration, or dilution, of the main input resource.

Typical Average Monthly Evaporation and Rainfall Rates in India and Australia						
Month	India			Australia		
	Evaporation	Rainfall	Net	Evaporation	Rainfall	Net
	mm	mm	mm	mm	mm	mm
January	154.57	0.11	154.46	368.90	36.20	332.70
February	150.80	0.00	150.80	301.00	56.10	244.90
March	185.40	0.00	185.40	299.15	55.25	243.90
April	190.54	0.00	190.54	232.50	13.10	219.40
May	225.17	0.00	225.17	172.05	51.55	120.50
June	202.65	95.76	106.89	124.50	47.75	76.75
July	148.27	162.56	-14.29	137.95	21.30	116.65
August	127.97	316.31	-188.34	173.60	12.50	161.10
September	155.69	141.24	14.45	237.00	1.80	235.20
October	164.76	0.00	164.76	310.00	1.40	308.60
November	161.48	0.00	161.48	337.50	2.30	335.20
December	156.99	0.00	156.99	370.45	4.15	366.30
Total	2,024.29	715.98	1,308.31	3,064.60	303.40	2,761.20

Table 3: Evaporation and Rainfall in Australia and India

Determine planned density and composition of saturated brine (maiden brine) to be delivered to the crystallisers.

It is well known that at a density of 1.2185 SG at 22.2°C. seawater-based brine will begin to precipitate sodium chloride. It is usual, therefore, to commence the transfer of brine to the crystalliser ponds at a density marginally less than saturation. This avoids precipitation at the transfer pump station and in the channel prior to the first ponds. In the absence of advice from the promoter of the field, it is assumed in the model that this transfer density will be 1.216 SG at 20°C. This brine is referred to as maiden brine.

Establish density and composition of brine to be discharged from the crystallisers as bitterns.

Using normal seawater as the source, 77.5 percent of the sodium chloride contained within the maiden brine will have precipitated from the brine when the density reaches 1.25 SG at 20°C. Beyond this density, increasing quantities of potassium, magnesium and sulphate ions will precipitate as contaminants of the salt bed. In Australia and Mexico, it has been found uneconomic in the past to upgrade the salt precipitated from brine exceeding this density. This brine is called bitterns. The first estimates therefore are usually prepared assuming this exit density. Research done at a number of saltfields has now confirmed that, as salt prices rise, it will be economically feasible to recover additional amounts of the residual sodium chloride remaining in the bitterns brine.

Establish formulae for tracking major elements in the brine as the brine concentrates through the concentration and crystalliser ponds, and calculate brine densities at which calcium, as gypsum, and chlorine, as salt, begin to precipitate.

The accuracy of the model depends upon tracking the amounts of each of the major elements remaining in the brine as it concentrates through the concentration and crystalliser ponds. The principal ions tracked are calcium, magnesium and chlorine. In the absence of site-specific data for seawater and concentrating brine analyses, Baseggio's data is used in construction of the formulae to be used in the models. A summary of Baseggio's data is shown in Table 4. Charts 1,2,3 and 4 show the density-concentration relationships for chlorine, calcium and magnesium.

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BASEGGIO Brine Analyses				
g lons/1000g brine in solution at 22.2°C				
sg (22.2°C/15.6°C)	Ca	Mg	SO4	Cl
1.0130	0.228	0.683	1.456	10.33
1.0272	0.442	1.409	2.876	20.89
1.0383	0.628	1.916	4.036	28.82
1.0516	0.806	2.546	5.392	38.34
1.0651	1.005	3.164	6.712	47.76
1.0757	1.170	3.687	7.805	55.56
1.0952	1.306	4.599	9.438	69.23
1.1123	1.134	5.456	10.29	82.21
1.1430	0.870	6.941	11.76	104.4
1.1669	0.683	8.072	12.87	121.5
1.1867	0.542	8.947	13.73	134.8
1.2076	0.408	9.936	14.79	148.9
1.2194	0.330	11.02	16.11	155.9
1.2217	0.312	12.48	18.05	155.2
1.2367	0.212	21.68	30.68	152.3
1.2462	0.160	27.05	37.89	151.1

Table 4: Baseggio's Brine Analyses

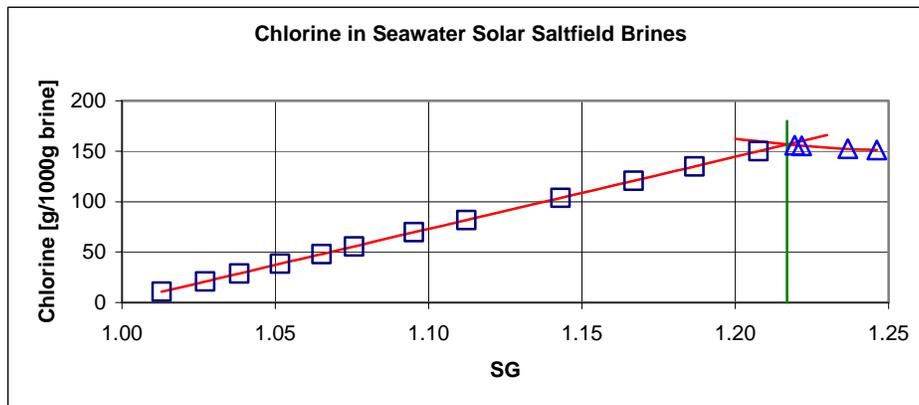


Chart 1: Baseggio Density-Chlorine Concentration

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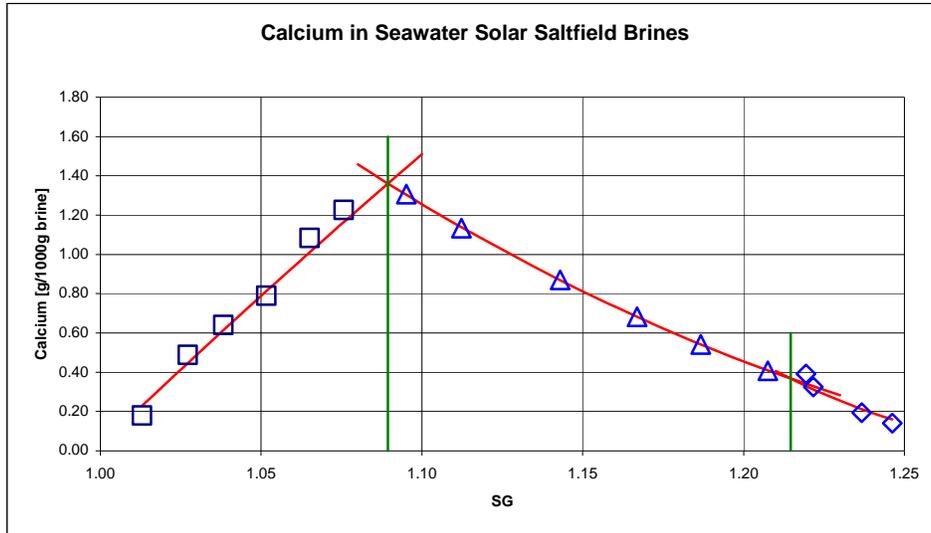


Chart 2: Baseggio Density-Calcium Concentration

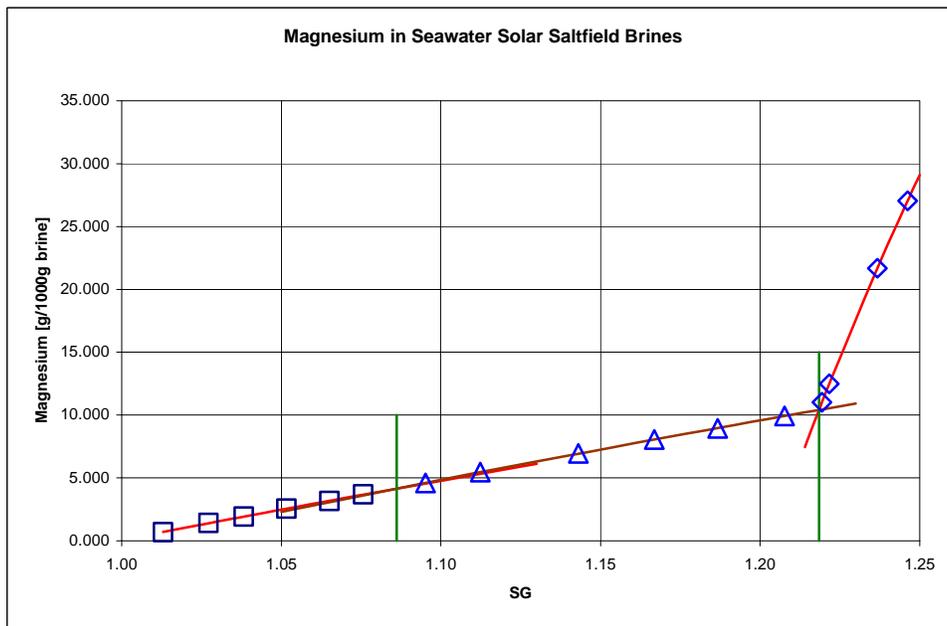


Chart 3: Baseggio Density-Magnesium Concentration

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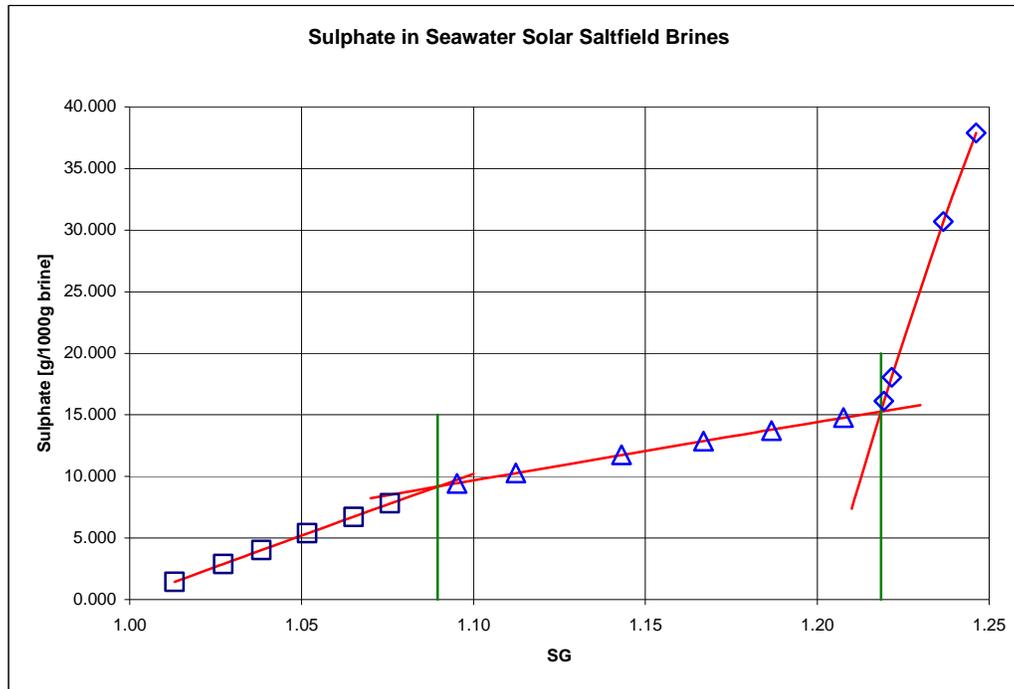


Chart 4: Baseggio Density-Sulphate Concentration.

Establish annual and monthly evaporation ratios for evaporation from brine in a pond to that of freshwater from a Class A evaporimeter, over the full range of brine densities from incoming seawater to outgoing bitterns.

As would be expected, as the concentration of dissolved salts increases, the brine density increases, the water vapour pressure is lowered and the evaporation rate decreases. However, the evaporation rates from large bodies of saline water are lower than would be predicted from evaporation rates from fresh water in a standard pan evaporimeter, when corrected for density alone. Due to the complexity of the interaction of the variables involved, no theoretical model has been developed that accurately predicts the evaporation rate from a specific body of saline water of a given density and for any given meteorological conditions. Even if such a theoretical model could be developed the comprehensive input data that would be required would probably not be available. The best method of predicting evaporation rates is to use measurements from existing saltfield ponds, ideally at the same or a nearby location.

The authors have been able to draw on their knowledge of the Western Australian solar saltfield operations to provide best provisional estimates of the evaporation rates. The Evaporation Ratio (ratio of evaporation from a saline pond to evaporation from a fresh water pan evaporimeter) varies from month to month over an annual cycle. The preliminary design is established using an estimated annual evaporation ratio of brine at salting point to that of freshwater in the Standard Class A evaporimeter. This ratio increases as the brine density decreases. The ratio at incoming seawater density is thus established. Subsequent refinements of the model incorporate estimates for the ratio for each month.

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Establish a value for probable run-off of freshwater into the concentration ponds.

Should the area under review be influenced by run-off of freshwater into one or more of the planned concentration ponds, then an estimate is made of the volumes expected. Where practical, run-off should be avoided.

Fix number of concentration ponds.

The number of concentration ponds required for any specific saltfield is not fixed. Issues to be considered include:

- Brine chemistry
- Brine biology
- Topography
- Economics
- Hydraulics
- Meteorological conditions
- Risk of catastrophic impacts such as cyclones, monsoons and flooding

Experience at other major solar saltfields in Western Australia and Mexico indicate that the optimal number of concentration ponds is in the range 7 to 10. The authors recommend 7 or 8 ponds for preliminary designs. As more data becomes available this recommendation may change, but is unlikely to be less than 7 or more than 9.

The theoretical basis of the mass balance model has been constructed to optimise both the overall size of the pond system and the control of the brine through the system. The actual size of each pond is determined after an assessment of the above factors and how best to fit the ponds into the available lease area.

Fix general layout of crystalliser ponds

The number and configuration of the crystalliser ponds involves an assessment of a number of factors, including:

- Evaporation rates
- Brine chemistry
- Topography
- Operational activities
- Harvesting methods

The two main systems used to configure the crystalliser ponds are the batch and the series systems. With the former, the saturated brine is fed to each crystalliser and is left to concentrate until it reaches the design bitterns discharge density. Up to two top-ups are made prior to a new batch of brine being introduced. This may necessitate a number of fillings each year.

In the series system, the ponds are configured into a series of two or three crystalliser ponds and concentrated brine is fed into the first pond of each series. As with the concentration ponds, the flow through a series system of crystalliser ponds is continuous, and a steady state brine profile is achieved through the system. The bitterns brine is discharged from the last pond of each series.

If the topography lends itself to gravity flow through each series, then the authors favour this system for control, production, minimal downtime and quality reasons.

Historically, it was assumed that the series system was optimised using three ponds in each series and decreasing the area down through the series. Over time, however, the marginal quality benefits achieved are exceeded by operational problems. Preliminary design, therefore, assumes a series system with two ponds in each series. All ponds are of the same size.

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Estimate rates of brine loss from horizontal and vertical seepage from each of the concentration and crystalliser ponds.

All solar saltfields incur losses of brine due to either vertical seepage through the pond floors, or to horizontal seepage through pond levees. Where possible, field geotechnical research should be undertaken to establish an estimate of vertical seepage losses through the pond floors. Should areas of potentially high losses be discovered, these should either be avoided when final levee alignment are made, or dealt with during construction.

Horizontal seepage losses can be best avoided by the use of optimal levee construction materials and techniques.

The brine mass balance model is flexible enough to enable several options to be run for a range of estimated seepage losses.

Select the optimum brine density for each concentration pond and each row of crystalliser ponds.

No absolute criteria have been established for determining the density gradient to be established throughout a series of concentration ponds. A frequent recommendation in the literature is to design for linear density profile, that is for equal increments in the exit density from pond to pond. This usually provides good control throughout the year in response to meteorological changes. The average density of the brine in any pond is approximately 99.5 % of the exit density

In addition to the linear density profile the authors used the mass balance model to analyse other density profiles. Three significant different options to the linear density profile have been considered:

- A concave density profile; the linear profile was adjusted to form a concave curve which decreases the inlet density to each pond whilst maintaining the seawater density to the first pond and the outlet density of the last pond.
- A convex density profile; the linear profile was adjusted to form a convex curve which increases the inlet density to each pond whilst maintaining the seawater density to the first pond and the outlet density of the last pond. Refer Chart 5.

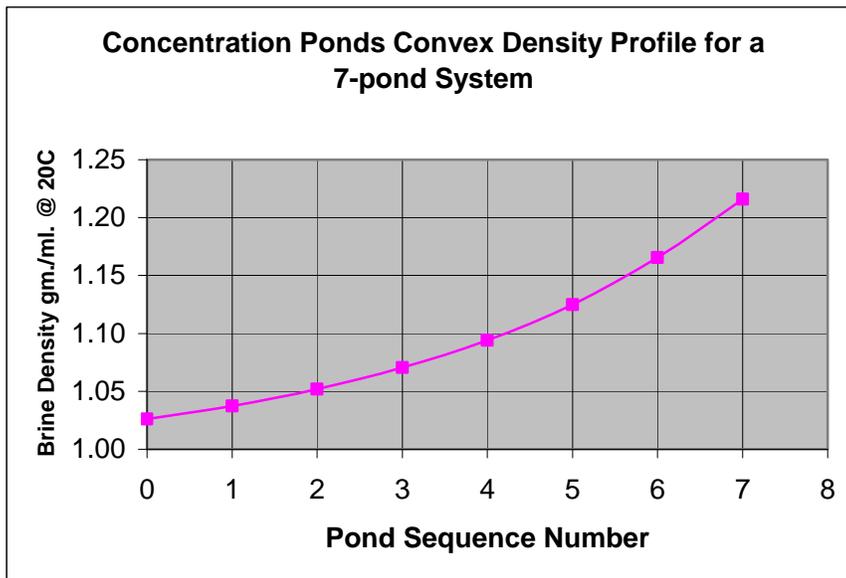


Chart 5: Typical Convex Density Profile for a 7-Pond Concentration Pond System

- A modified concave density profile; the inlet density into Pond 3 was adjusted to be less than 1.087 gm./ml. which is the density at which calcium, as gypsum, commences to precipitate.

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The density profile selected for one field in Australia was the “modified concave”. It was found to minimise the area of concentration ponds required while providing good operational control and ensuring that no problems would occur due to premature deposition of gypsum

Estimate the annual volume of seawater to be delivered to the concentration ponds

Based upon the average seawater density an estimate is made of the annual volume required to provide the volume of maiden brine from which the required amount of NaCl will be precipitated in the crystallisers; assuming discharge density of the bitterns brine will be 1.25 SG. Running the model using this input will provide estimates of pond areas and product output.

Run model and adjust input seawater volume until output salt is that required.

The model is then run until the target output is achieved through adjustment of pond areas.

Adjust the areas of concentration and crystalliser ponds to best fit the available terrain..

Adjustments to individual pond areas are then made to take into consideration actual topography and possible areas of high seepage losses.

Freeze the target pond areas and recalculate the annual mass balance to determine the density profile.

The revised pond areas are now frozen and the model is re-run to establish the final density profile.

Expand the mass balance model to calculate monthly flow rates for the fixed pond areas.

The model is now expanded so as to calculate the monthly seawater and brine flow rates. This requires an estimate for each month of the evaporation ratio, based upon the monthly freshwater evaporation and rainfall

CONCLUSION

The global demand for high-quality solar salt for edible use and for chloralkali production has recently exceeded supply; specifically in China. This shortfall in demand has been met by the rapid increase in output of vacuum salt produced from underground rock salt deposits in China. The production costs for this salt far exceed those of solar salt. Demand for caustic soda in China has grown from less than 4 million tonnes in 1995 to more than 12 million tonnes in 2007. Production of caustic soda in India is currently around 2 million tonnes. If demand for chloralkali and soda ash in India grows at rates similar to those experienced in China, then the demand for salt to service this growth should preferably come from new solar saltfields; supplemented by improved productivity and quality from existing fields. India does not appear to have the option that China has in developing domestic rock salt deposits.

The benefits to be obtained from use of the brine mass balance models developed by the authors and described above include:

- Optimal utilisation of available area
- Optimal design of the pond system
- Reduced capital costs
- Operational control efficiency
- High productivity
- Flexibility to adjust rapidly to changes in weather conditions
- Continuity of high quality production
- Reduced operational costs
- Options for further recovery of salt.

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In association with Salt Partners Limited, the authors can provide a one-stop option to clients wishing to develop new solar salt facilities. They can also work with the operators of existing facilities seeking to optimise productivity and quality of the salt production process.

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