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Brine Quality Management in Solar Salt Operations

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ABSTRACT

The nature of site-specific brine quality problems experienced by Dampier Salt at two large solar salt fields in the north west of Western Australia are detailed. Lake MacLeod produced opaque salt with high levels of occluded moisture due to high concentrations of trace metals in the brine. Dampier produced very soft hopper-shaped salt high in calcium, as a result of viscous brines caused by biological disturbances. The research findings which enabled the Company to identify and eliminate these problems are presented together with details of the improvements in salt quality that were achieved at both salt fields.

INTRODUCTION

Dampier Salt (Operations) Pty Ltd operates two large solar salt fields in the north west of Western Australia. The salt field at Dampier produces about 2.5 million tonnes of salt per year from the concentration of seawater pumped from the Indian Ocean. The salt field at Lake MacLeod produces about 1.5 million tonnes of salt per year using pre-concentrated subterranean brine as a brine source. Each of the salt fields has, historically, experienced distinct salt quality problems which have been eliminated by the application of research findings. The problems experienced are common to many salt fields throughout the world. This paper details the nature of the problems experienced at each salt field and the methods used to overcome them and ensure that they do not recur.

SECTION 1: LAKE MACLEOD

Lake MacLeod is a 2000 km^2 natural coastal salina situated 40 km north of Carnarvon in the north west of Western Australia. It is separated from the Indian Ocean to the west by a limestone ridge about 15 km wide and to the south by a 2 km barrier of white dunes. The evaporite sedimentation and basin evolution has been extensively researched by the University of Western Australia (Logan, 1982). Their findings show that free exchange of seawater with the ocean ceased about 5300 years ago, although there is still substantial seepage of seawater into the lake through the porous rocks of the barrier. The seepage is driven by hydrostatic differentials of 3–4 m, maintained by permanent imbalances between inflow into the basin and evaporation from the surface (majanna environment). This imbalance has, in turn, led to the development of a 10–12 m thick lensoid body of evaporite salts deposited in a large basin in the southern portion of the lake called the MacLeod evaporite formation. The principal salt is halite with subordinate gypsite and calcite. The evaporites are mixed with and overlain by sediments. Intrastratal brines are recharged by infiltration, from periodic brine sheets which flood across the surface of the lake.

The Lake MacLeod salt field utilises intrastratal brines which seep into a "collection" channel excavated into the halite evaporites. These brines are saturated with sodium chloride, but are also rich in nutrients and initially acidic with a strong smell of H_2S gas. This brine is pumped into a "feed" channel where it becomes aerobic and the pH rises spontaneously to about 7.2. It is then channelled directly into crystallisers.

If the brine was not chemically treated it becomes intensely red due to the growth of beta-carotene rich microalga *Dunaliella salina* and associated red halophilic bacteria. The red brines increased solar evaporation by about 15% but the salt produced was of low quality, being opaque and containing high levels of occluded moisture. The *Dunaliella salina* was at first thought to be responsible for the poor quality salt due both, to reports in the literature (Davis, 1980a,b), and the fact that red brines containing this algae in other salt fields and salinas, had similar poor quality salt.

The removal of *Dunaliella salina* from the brine did not, however, solve the problem and it became obvious that the factor causing the problem was present in the brine at its source. This factor was later identified as a trace metal which could be controlled by pH adjustment. The treated brine grew extremely high quality salt. Subsequently, the pH of all field brine was then elevated using caustic soda addition. Table 1 compares the quality of salt grown from treated and untreated field brines shipped during 1985. Total moisture content had reduced by 1% with a corresponding 1% increase in NaCl content. Occluded moisture had halved with corresponding decreases in magnesium content.

TABLE 1

Comparison of total salt shipped in 1985 from untreated and treated brines at Lake Macleod

	Untreated brine	pH adjusted to 8.1
NaCl %	96.26	97.34
H_2O %	3.43	2.41
Ca %	0.044	0.039
Mg %	0.030	0.019
Na %	37.87	38.29
K %	0.014	0.012
Cl %	58.48	59.12
SO_4 %	0.144	0.111
Insoluble %	0.015	0.011
Occluded H_2O %	0.97	0.54

The elevation of brine pH directly inhibited the growth of red halophilic bacteria. There was also some precipitation of phosphate from the brine which reduced the population of *Dunaliella salina*, resulting in a clearer brine.

High levels of trace metals, including manganese, occur in the acidic interstitial brine beneath organic black muds, that typically accumulate in the primary ponds of most solar salt fields. This brine can sometimes be forced via hydrostatic pressure into adjacent crystallisers, constructed at a lower level than the primary ponds. The inflow of brine often produces dark holes which appear in the salt floor of the crystallisers, where the salt has dissolved in the low density incoming brine. The salt produced in these crystallisers tends to be opaque and of low quality. This has implications in salt field design.

SECTION 2: DAMPIER

Technical details of the solar salt field at Dampier have been published by McArthur (1980), and a description of the biology by Sammy (1984). The brine concentrating ponds are homogeneous and maintained at constant brine density by adjustment of pumping rates thus appearing to be in a steady state. There is, however, deposition of salts from the through flowing brines reflecting the essentially dynamic nature of the ponds from the chemical composition view point. A model of the salt field at Dampier is presented by Burnard (1992) at this conference.

Numerous papers have been written on the effect of biology on salt production (Davis, 1980a,b; Jones et al., 1981; Sorgeloos, 1983; Sorgeloos et al., 1986). These are all, however, broadly based on the pioneer model published by Davis (1980a). Since this time there has been little addition to the fundamental published understanding of how the biology effects salt production.

The salt field at Dampier experienced biological problems in the early 1980s which had serious effects on salt production. These problems could not be explained or solved on the basis of published information. An intensive research programme into the biology, chemistry and crystallography of the salt field was then undertaken. The fundamental causes of the salt quality problems, which had previously been misunderstood, were identified. A number of steps were then taken to remedy the problem and ensure that they did not recur.

CAUSES OF SALT PRODUCTION PROBLEMS

It is well known that the proliferation of a unicellular cyanobacterium now called *Synechococcus* (Ripka et al., 1981), previously called *Aphanothece halophytica* and *Coccochloris*, can cause severe salt production problems (Davis, 1980a,b; Jones et al., 1981; Sorgeloos, 1983; Sorgeloos et al., 1986). It was suspected that the problems were related to the large amounts of extracellular polysaccharides produced by this organism (Jones and Yopp, 1979; Davis, 1980b; Hall and Fischer, 1983; Sammy, 1984; Yopp et al., 1978) which elevate brine viscosity (Davis, 1980a,b; Jones et al., 1981; Sorgeloos, 1983; Sammy, 1984; Sorgeloos et al., 1986). It was believed that the organic material produced by this organism directly interfered with salt deposition and that evaporation was inhibited by viscous brine, decreasing salt production (Davis, 1980a,b; Jones et al., 1981; Sorgeloos, 1983; Sorgeloos et al., 1986).

Our studies indicated that elevated brine viscosity directly affected crystal shape but did not significantly reduce evaporation. The organic content of the brine elevated viscosities but did not appear to directly interfere with salt deposition. Brines could be chemically treated to break the long chain polysaccharide molecules, thereby reducing viscosity without altering the total organic carbon content of the brine and allowing high quality salt to be grown. The nature of the organic material was, however, changed by the chemical treatment and it is possible that the organics in their original quantity and form, did contribute to the modified crystal structure. High levels of organic material were bound up in the crystal matrix of the salt grown in the high viscosity brine which went brown when heated to 400°C. High brine viscosities decrease salt production indirectly by causing banks of drift salt which accumulate on the perimeter of the crystallisers and reduce the evaporative surface area. This will be discussed in detail later.

The fundamental cause of salt production problems at Dampier was high viscosity brine caused by dissolved extracellular polysaccharides originating from slime producing microorganisms. These micro organisms inhabited ponds in the brine density range 1.10 to 1.16 g/cm^3 and included both *Synechococcus* and a number of species of purple photosynthetic bacteria which normally occur in stable microbial mats. Changes in conditions in the ponds caused the microbial mats to become unstable and begin to lift off the floor of the pond. The agitation of microbial mat (containing polysaccharides) in the brine column caused brine viscosity increases. It was found that the polysaccharides would only be released into the brine in significant volumes under these notable conditions and that a stable microbial mat did not elevate the brine viscosity regardless of the amount of polysaccharide it contained. The problems were therefore caused by factors destabilising the microbial mats.

The solution therefore involved identifying the conditions necessary for stable microbial mats and managing the salt field to ensure that these conditions were maintained in the critical ponds.

STABILITY OF MICROBIAL MATS

Two major factors were identified as being critical for stable microbial mats in the brine ponds at Dampier. These were, high light intensities at the pond floor and the correct type of substratum. A brief summary of these factors and their influence follows.

High light intensities

High light intensities are essential for stable microbial mats, which generally occur in brine less than 10 cm deep (Birke, 1979). At Dampier the microbial mats on the floor of a 40 cm deep pond containing brine of density 1.13 g/cm^3 disappeared in late 1983 when brines became very turbid. The floor of the pond could not be seen under 10 cm of brine. The mats began to regrow when the brines cleared and they became increasingly stable with increased brine clarity.

They are now very stable and light intensities of over 20,000 lux reach the pond floor at noon, during summer. The stability of the microbial mats appears to be related, at least in part, to a layer of purple photosynthetic bacteria that occurs below the surface layer of cyanobacteria and above a layer of decomposing mat generating H_2S gas. Purple photosynthetic bacteria become immotile and produce large amounts of cohesive slime when subjected to high levels of light and sulphide (Pfennig, 1977). High levels of light therefore tend to increase mat stability.

High levels of light at the pond floor are achieved by shallow clear brine. Brine clarity can be increased by limiting the growth of phytoplankton via a minimisation of nutrient input. It can also be increased by introducing the Brine Shrimp, *Artemia*, which remove all particulates in the size range 3–50 microns (Persoone and Sorgeloos, 1980)

Substratum

It was found that organic mud and clay substrata supported microbial mats which were cohesive and structured. Microbial mats overlying gypsum were soft, unstable and unstructured. This was particularly so if gypsum was still being precipitated.

It became apparent that the history of a pond was very important. If a pond had been used to contain high density brine and had grown a gypsum floor; this would not dissolve, at least not in the short term, when the brine density was lowered. It is possible, therefore, to irreversibly change the nature of a pond and create long term biological problems. It is also very important to limit the input of nutrients (phosphates and nitrates) to ponds where gypsum is being deposited.

EVENTS LEADING TO BIOLOGICAL DISTURBANCES AT DAMPIER SALT

The amount of salt produced by a salt field in an average year can be increased by increasing the evaporative surface area. In the case of the Dampier Salt operation, all ponds have a fixed surface area except for the first pond (Pond 0). The evaporative surface area of Pond 0 was increased from 3,500 ha up to 5,200 ha in anticipation of an increased demand for salt in late 1979/1980. This gave a brine density increase in the pond from about 1.040 g/cm^3 up to 1.060 g/cm^3. Elevated brine densities caused the death of a variety of fish and seaweeds that could not tolerate the new pond conditions. This, coupled with nutrients entering the brine from newly flooded mudflats, resulted in a plankton bloom. Nutrient bound up in plankton and dissolved in the brine column passed downstream and entered a pond containing a stable microbial mat and *Artemia*. The population of *Artemia* in this pond initially increased in line with an increase in the supply of microalgae food and the brines remained clear.

The brine density of the pond rose from about 1.10 g/cm^3 up to 1.13 g/cm^3 in line with the new operating parameters of the salt field. This resulted in a precipitation of fine gypsum particles raining onto the stable, laminated microbial mat throughout the pond. The mat surface microorganisms, mainly *Synechococcus*, grew up through the layer of depositing gypsum as an unstructured and unstable assemblage of microorganisms growing on top of a gypsum crust. The gypsum crust formed as the result of the fusion of small gypsum crystals in the layer of decomposing mat, beneath the actively growing surface layer. The instability of the mat community resulted in pieces of mat material tearing off the pond floor and being agitated in the brine column. This agitation released polysaccharides and elevated the brine viscosity. The higher brine densities also stimulated additional polysaccharide production from the *Synechococcus*, (Yopp et al., 1978 and unpublished data) and caused further increases in brine viscosity. *Synechococcus* which can also proliferate in the brine column, (Davis, 1980b; Yopp et al., 1978; Sammy, 1984; Jones et al., 1981) became planktonic. The brines in the ponds became increasingly turbid further reducing the stability of the microbial mats and exacerbating the problem. Overall algal productivity remained high due to the input of nutrients from upstream ponds.

Artemia obtain no nutritional benefit from *Synechococcus* (Davis, 1980b and unpublished experiments conducted at Dampier Salt). They also expend much more energy in swimming through viscous brine. This started a decline in the *Artemia* population of the pond. *Artemia* were then eliminated completely in late 1982, as the result of a mass precipitation of calcium carbonate/calcium sulphate crystals which turned the brine milky. These crystals were ingested by the remaining *Artemia*, causing death. These effects were verified in laboratory tests. The reasons for the formation of milky brines are still not fully understood. The brine quality situation then became critical with very turbid, viscous brine and virtually no microbial mat, but with high productivity of planktonic *Synechococcus* in the brine column. This, in turn, lead to the severe salt production problems described below.

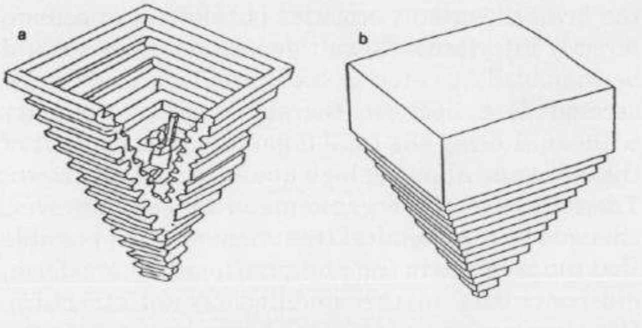

Fig. 1. Effect of brine viscosity on salt crystallisation. (a) Salt from viscous brine — hollow hopper-shaped crystals with step and sheet-like growth; (b) Salt from normal brine — solid cube-shaped crystals.

EFFECT OF BRINE VISCOSITY ON SALT PRODUCTION

High brine viscosity prevents the efficient circulation of brine through wind action and density inversion resulting from surface brine becoming denser, due to evaporation. This causes excessive salt particles and sheets of salt to form on the brine surface, which eventually sink to give large numbers of salt crystal nucleation sites, on the floor.

Another result from high viscosity brines containing long chain polysaccharide molecules is the change in salt crystal morphology from solid cubic growth to hollow, skeletal hopper shaped crystals. The modification effect of the polysaccharide absorption and ion depletion at the crystal growth faces causes preferential growth at the lower energy cube edges and corners, causing the hopper salt growth (Fig. 1). These types of crystals have also been reported by Baha Al-Deen (1972). The overall effect of hopper crystal growth, interference from adjacent growing crystals and fine salt deposition is the production of misshapen lower bulk density crystallised salt.

Gypsum crystals which continue to deposit in the crystallisers can become trapped within the hollow salt crystals and are not readily removed by the normal washing process. The hollow salt, coupled with increased calcium input into the crystallisers, caused an elevation in the calcium content of the washed product.

Thin sheets of salt formed on the brine surface are also transported by wind action to the pond peripheries and accumulate as drift salt banks. This encroachment from four sides greatly reduces the evaporative surface area of the crystallisers resulting in decreased salt production.

The build up of drift salt banks in crystallisers containing viscous brine begins from the time of flooding and steadily increases until harvest time. Brines at Dampier Salt were at their most viscous in 1984 with viscosities elevated about 20% above normal. This resulted in a significant portion of the crystalliser surface area being reduced by drift salt and was responsible, at least in part to, a lowering of the bitterns discharge density. Salt that was deposited was relatively soft and had low bulk density.

The main differences in the quality of salt grown from viscous brine and normal viscosity brine was in as-washed moisture content and level of calcium. Moisture content of salt after washing was over 10% compared to current levels of less than 5%. Typical calcium levels reached 0.1% compared with the current 0.03% Ca. Unwashed salt produced from the viscous brines had a calcium content of about 0.2%, which was slightly higher than the current 0.16%; however, the percent removal of calcium was only about 50% compared to the current 85–90%. This was attributed to the modified crystal shape and the increased proportion of fine salt which was difficult to wash.

SOLVING THE PROBLEM

The solution to the brine viscosity problem involved chemically treating the brines to return the brine viscosity to normal, until the management of the pond biology limited the input of polysaccharides to the brine, making it unnecessary to continue chemical treatment.

Chemical treatment

Initial experimentation involved the removal of polysaccharides from the brine by reverse osmosis and chemical flocculation techniques, which were effective but difficult to apply on a large scale. Test work showed that the viscosity of the brine could be returned to normal using chlorine. This patented process breaks the long chain polysaccharide molecules (greater than 20,000 Daltons) into smaller molecules without altering the total organic carbon content of the brine. The result is a physical reduction in brine viscosity. The amount of chlorine required was found to be directly proportional to the amount of dissolved polysaccharide allowing a reduction in chlorine addition as the pond biology stabilised, to the point where it was no longer required.

Biological management

The biological solution to the problem involved reducing the surface area of the salt field to minimise nutrient input from upstream ponds and to reduce the brine density and consequent gypsum deposition in the problem pond. This was, to some extent, necessitated by the need to balance the primary pond area with the then reduced crystalliser area. *Artemia* were mass cultured in constructed pools and routinely added to the field pond for 18 months, until the *Artemia* were re-established. Additionally, the problem pond was divided into three separate sections to ensure that all gypsum was deposited in the last section. The removal of nutrients from the brine by biological communities in early ponds limited algal productivity in this section and when coupled with increased gypsum deposition, resulted in slime producing microorganisms being buried in the gypsum and no longer causing problems.

The change in the nature of the pond floor from clay to gypsum that had occurred was not reversible in the other sections of the pond no longer experiencing gypsum deposition (at least in the short term). This prevented a complete return of the stable microbial mats present in these areas prior to gypsum deposition. Mat stability did, however, improve dramatically with corresponding decreases in brine viscosities to low levels. The residual viscosity elevation was easily reversed by downstream chemical treatment of the brine.

The deposition of gypsum is affected by biological conditions. Without biological influences gypsum deposits at a brine density of 1.086 g/cm^3 (Baseggio, 1974). At Dampier deposition occurs at about 1.100 g/cm^3 and in a Queensland salt field, at 1.13 g/cm^3. This is believed to be due to a biological interrelationship with calcium in the brine system causing the density at which calcium sulphate deposits to be raised. This has implications in salt field design because without knowledge of where gypsum will deposit, it is difficult to determine the design salinities for the middle salinity ponds.

CONCLUSIONS

Critical points in maintaining stable microbial mats are as follows:

1. Minimise nutrient input to middle salinity ponds, especially those where gypsum is depositing.
2. If nutrient input cannot be avoided, it should enter the system as early as possible to maximise the chance of it being utilised in ponds upstream of the potential problem areas.
3. Design ponds that are relatively shallow.
4. Maintain pond conditions as constant as possible to enable stable communities to develop.
5. Introduce *Artemia* to clear the brine column.

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