

## Changing Waste Irrigation Waters from Pollutant to Beneficial Products: A Study of Recovery and Use of Salts from the Salton Sea

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### Abstract

The Salton Sea in Southeast California receives irrigation and domestic drainage containing large amounts of mixed salts including nitrates. Evaporation has concentrated the salts to 25% higher than seawater. Much of the Sea is shallow and warm weather fosters algae blooms that result in large kills of fish and wildfowl. Reversal of these conditions requires the removal of salts at some rate greater than the inflow. Much of the salt content is beneficial to agriculture and should be returned to the areas of farmland that needs them. Huge needs for common salts are accumulating because the present prices for the salts are too high.

These exploratory tests indicate that the excess salts can be recovered by solar evaporation and winter chilling into usable crude salt components at the low costs required for wide scale use in treating soils. Rural communities will benefit and the Salton Sea will again be a fine recreational area.

### 1. Background

The Imperial Valley area in which the Salton Sea lies was once part of the Sea of Cortez. It was cut off by the spreading delta of the Colorado River and dried up to become a large depression. Flooding of the lowest part started with a canal breaking in 1906. Irrigation drainage and other inflow has increased the surface area of the Salton Sea (SS) to 381 square miles (98,700 hectares) at an elevation of 227 feet (69 meters) below sea level [1]. Irrigated land on the periphery of the depression receives 3 million acre feet ( $3.7 \times 10^9$  cubic meters)/year of Colorado River Water with a salinity varying around 700 PPM TDS. The SS itself receives 1.3 million acre feet ( $1.6 \times 10^9$  cubic meters) of irrigation drainage and other runoff. The incoming salt concentration is about 4400 PPM TDS for an inflow of over 3.6 million metric tons of mixed salts per year. Evaporation has raised the levels of salts to 44,000 PPM TDS of which about 900 PPM is  $\text{NO}_3$ . The nutrient content of the water is so high that warm weather triggers algae blooms, usually in shallow areas, that deplete the oxygen causing massive fish kills. Large numbers of wildfowl also perish,

possibly because they eat the decomposing fish. No evidence of excessive levels of pesticides or of selenium above 1 PPB has yet been recorded. Work is underway to save the wildfowl and fish habitat and to return the Salton Sea to its former status as a prime recreational area. Government funding probably will include only provisions for "landfilling" the recovered mixed salts.

This preliminary report is part of an ongoing private study [2] to see if it might be possible to convert these waste salts to beneficial use through private enterprise.

### 2. A Source for Low Cost Salts.

The existing rail, highway, and power infrastructure and the option of enclosing areas of the Salton Sea for the ponds allows a very low cost installation as compared with most solar salt works [3]. Use of the salts in or near to the area of origin reduces freight costs, and equally important, reduces the use of fossil fuels in transportation. The costs can be further reduced by producing less stringent specifications suited to the new markets.

### 3. Uses for Crude Salts

Calcium Sulfate, as gypsum, produced by mining or as an industrial by-product, is widely used in leaching irrigated fields to remove excess salinity. Calcium carbonate in the gypsum may assist modestly in the leaching of sodium and by reaction with sodium sulfate.

Magnesium Sulfate shows promise for use in leaching saline lands provided that a minimum of calcium sulfate is present. Sodium Sulfate at low cost is sorely needed to combat Texas Root Rot" in the Southwest U S and Northwest Mexico. College Station (Texas A & M) started working on the root rot problem in 1886. Dr. Stuart Lyda found the cause around 1970 [4]. A fungus flourishes in soils so impervious to gas movement as to retain much of the carbon dioxide from decaying humus. These soils have low porosity and permeability because of a high calcium carbonate content and lack of the sodium needed for swelling when irrigated. The fungus starts acting as carbon dioxide contents in the soil atmosphere rise above 3.15 to 3.2%. Increased soil permeability cures this problem and sodium provides the swelling characteristics to increase the porosity and permeability. Diagnosis of the problem is necessary for success. The author sold hundreds of tons of sodium chloride to knowledgeable farmers for remediation of calcium carbonate soils and in every case it worked well. However, the practice fell into disrepute when farmers started throwing salt onto bare spots without first checking to see if the problem was root rot or an already excess salinity.

One farmer reasoned: "why not, the land was not growing anything anyhow". This undisciplined usage of sodium chloride led to a lot of "it did not work for me" comments. Objections to adding chlorides that would end up in irrigation drainage also caused the use of sodium chloride for root to dwindle.

Some farmers have continued their success by periodically applying salty drainage on the root rot areas or water from irrigation welts that were once idled when they turned salty. Applying the needed sodium as sodium sulfate avoids the chloride problem and the sulfur has an added value as an essential plant nutrient; but the cost has always been too high. Crude sodium sulfate can be recovered from the Salton Sea at minimum cost to meet the needs of the 'root rot area' that extends from the Colorado River area to East Texas and south into Sinaloa, Mexico. These soils respond not only to the sodium ion but react positively to the application of sulfur or sulfate ion that is even sparingly soluble: Gypsum soils do not support root rot. Magnesium sulfate, as an impurity in the sodium sulfate, supplies highly soluble sulfate and the magnesium added to the soil is of no consequence as compared with the effects of calcium and sodium.

Thus the most troublesome separation associated with bitterns, closely separating the sodium and magnesium sulfates, is avoided. The use of less pure forms of sodium sulfate also appears to apply to its use for energy storage in the range of about 18to31°C.

Crude sodium chloride can be utilized to good effect for stabilization of soils in foundations and roadbeds. Bitterns are useful for dust control.

Table 1  
Ions As a Weight Percentage of the Total Ions in the Initial Brine

Source	Ocean	Great salt Lake	Salton Sea
Sodium, Na	30.8	32.6	27.9
Chloride, Cl	55.3	55.8	39.2
Sulfate, SO <sub>4</sub>	7.8	6.6	24.2
Calcium, Ca	1.2	0.2	2.4
Magnesium, Mg	3.7	3.1	3.3
Carbonate, CO <sub>3</sub>	0.3	0.2	0.3
Nitrate, NO <sub>3</sub>	—	0.1	2.6
Do not total 1005 due to rounding			

With this many good uses for the salts there is no reason or acceptable excuse for 'landfilling'.

4. Using Weather Energy to Lower Costs. A few exploratory evaporation and chilling tests have been conducted to provide a first look before starting a larger program. That program will truck brine from the Salton Sea to larger test ponds at our Dale Lake operation about 60 air miles due North of the SS. Dale (dry) Lake has a natural underground brine saturated at 22.3% sodium chloride, 7.2% sodium sulfate. It was operated from about 1939 through 1947 for sodium sulfate with sodium chloride as a by-products. Winter chilling of brine separated much of the sodium sulfate which was later dissolved and then crystallized by solar evaporation. Our previous work in producing 99.9+ NaCl from salt wastes at Searies Lake and Dale Lake [5] prepared us for work with high sulfate brines. A cautious approach is necessary. Brines high in sodium sulfate are very sensitive to both the high and low ends of the 15 to 25 °C daily differences between night and day temperatures common in arid areas. The difficulties increase as the ratio of chloride to sulfate ions decreases.

The ratio ( by weight ) for the Great Salt Lake of Utah is typically 8.45/1 [6], seawater is typically about 7.1/1 [7], and Dale Lake is 2.7/1, but the Salton Sea chloride/sulfate is only 1.3/1 Salts collected from San Joaquin Valley Evaporation Ponds have reverse ratios with the sulfate/chloride running from 2.2/1 up to 27/1[8]. The traditionally large difference between the cost of sodium sulfate and sodium chloride will lessen as we learn to manipulate the high sulfate brines. First trials were run in early July to get results representative of the higher summer temperatures. A second trial was run in late September as the night temperatures started to fall.

Tests were run so as to roughly duplicate the typical solar practice of at least 3 evaporation stages used in series to get best evaporation efficiency.

Evaporation was carried out in duplicate pans 33cm X 63 cm X 10cm deep, lined with polyethylene film. Daily ambient highs were 38-42 °C and night lows were 15° to 17°C less. Daytime relative humidity was 15 to 25%. The specific gravity (sg) of the Salton Sea water was 1.03 as measured by hydrometer.

On the second day of evaporation (sg 1.047) white

flakes were forming with many floating on the brine surface. By morning of the third day, at (sg 1.057), the flakes formed an almost continuous covering. The evaporation rate varied between 0.9 and 1.2 centimeters per day until the specific gravity was at 1.145 and the floating crystals, now including other salts, formed a thick continuous skin that hindered evaporation. Before the skin formation the brine temperature daily highs were in the range of 22 to 30 °C. After a continuous skin formed on the surface the brine temperatures were as high as 48 °C. At this point, sg 1.145, about 75% of the precipitate in pan 'B' was taken for analysis and allowed to drain but was not washed. It analyzed 17.8% Ca, 0.8% Mg, 0.51% sulfate, and 0.18% potassium. It is assumed that this is mostly calcium carbonate and that most of the magnesium, sulfur, and potassium came from the brine that did not drain from the sample.

Evaporation was continued to sg 1.22 and a salt sample was taken from the pan that had much of the calcium solids removed for the first analysis. The crystals were generally small with none larger than 3 mm..

This sample was rinsed for 10 seconds with an equal weight of the starting brine and then allowed to drain indoors for 3 days. This was the only 'hashed' sample in either run. The analysis, dry basis, was; Ca, 0.058%. Mg, 0.357%. SO<sub>4</sub>, 0.021%. and K, 0.137%. This indicates that washing procedures common to salt works could be used to produce some commercial quality salt. Two additional sets of salt samples were taken from each pan, the first set at about 75 % evaporation and the next at about 85%. In these two samples we found, respectively, magnesium at 2.2 and 3.7 %, sulfate at .23 and .20%, and potassium at 0.653 and 0.865%. (The low sulfate analyses were not expected and the analysis must be rechecked.)

Some of the bitterns did not evaporate to dryness even under these hot dry conditions proving their value for dust control on the dirt roads common in Southern California. A second run using the same pans and a similar procedure was made in late September as the nights started to cool. Analysis of the recovered salts followed the pattern of the first tests. All salt samples contained more than 90% sodium chloride and are suitable for soil stabilization. (The salt from these and

other runs will be accumulated for use in tests to see how a new method [see Appendix] for refining salts works on such complex materials.)

One liter of the remaining brine (sg 1.342) was further evaporated outdoors until a level slightly above 520 ml. total of brine and settled salts was reached. Some of the precipitated salts had adhered to the glass above the brine level and are not included in this volume. The brine was drained and 480 ml. was recovered at sg 1.293. Despite the evaporation of over half of the water, the precipitation of the salts due to temperature changes had lowered the specific gravity of the brine.

This 480 ml was divided into 100 ml. and 380 ml. splits. The 100 ml was transferred to a 200 ml beaker which was then sealed with plastic wrap to avoid evaporation. It was then cooled by refrigeration in a compartment at 4.4 °C. The wrap was removed only for as long as it took to measure temperature with a thermometer that was also kept in the refrigerator. The first precipitation of fine crystals was noted at 14 °C. Cooling was continued overnight in an iced compartment. The morning temperature was 2.2 °C. The fine precipitate had caked at about 45% of the total volume. A stir spatula was used to break the cake into fine particles which were allowed to settle. The settled level was about 40% of the total volume. The liquid was drained and the wet solids were heated in a microwave oven for 3 to 5 second intervals to avoid overheating and evaporation. At 20 seconds total heating time the crystals had melted enough to allow temperature measurement (30.5 °C) In 7 minutes it dropped to 27.7 °C and held. This was the apparent melting point of the crystals in contact with that brine.

Brine hardness was measured using a Hack Kit 5B and the procedure used for checking brines used in water softening [9]. It was 1020 grains calculated as calcium carbonate. The 380 ml split was placed into a ceramic bowl, sealed with a thin clinging plastic wrap, and put out to chill overnight. The air temperature was 14°C at midnight and 10 °C at 6:10 AM. The sample temperature was 9.5 °C. The volume had not measurably decreased so the indication is that the night low was cooler than the 6:10 AM temperature. The brine in the bowl appeared to be unchanged but actually contained many crystal-clear acicular crystals 4 to 6 cm. long. These were removed with a table fork, drained, weighed, then placed on filter paper for blotting some of the adhering brine. The blotting removed an additional 3.5 grams of brine. The drained

and blotted weight was 58.1 grams and the sg of the brine was 1.254. 40 grams of these crystals were placed in a 125 ml sample bottle and heated in the microwave for short increments to initiate melting. The 'hold temperature' was measured, the liquid was then drained from the bottle, and a hardness measurement made on the drained liquid. Four cycles were completed. Each time the hold temperature was 27.7 °C. The hardness equivalents of the melts were 1320, 2100, 1500, and 1500 respectively. It is surmised that the crystals are sodium sulfate containing 2-3 % of magnesium sulfate and minor amounts of other salts.

The remainder of the brine was stored in the refrigerator for future analysis. More crystals will be collected in like fashion for closely determining heat of melting so that their use as a medium for heat storage may be fully evaluated.

##### 5. Sodium Sulfate for Energy Storage.

Sodium sulfate deca-hydrate is the most widely studied material for storing phase change energy because it is effective at temperatures within our daily experience, say from refrigeration at 4 °C to warm water at 31°C. Patents and professional papers have been abundant for 50 years and these sources tell all that is needed for effective use in many applications. There are additives to sodium sulfate to overcome its tendency to form crystals that do not melt reversibly and other additives to vary the point at which the phase change occurs.

Uses extend from filling water bottles to keep one's feet warm to heating entire living and working spaces. For heat storage at higher temperatures, anhydrous sodium sulfate undergoes a phase change at 241 °C with the absorption of 27 BTU/lb (15 cal./gm.) of material. Using pellets of the anhydrous material to recover heat from flue gases and other waste heat sources offers a major opportunity to transfer waste heat at that very usable 241 °C.

Thirty years of the patents have expired so there is no barrier to using the information needed to put heat storage into practice. Once again the remaining barrier is cost and availability of the materials.



## 5. Conclusions.

The good news is that there does not appear to be any technical obstacles to recovering usable salts from the Salton Sea. The numerous professional papers published on reclaiming salts from bitterns are ample evidence of the know-how available within the industry. This know-how need only be extended to this new class of bitterns.

This report of exploratory work is meant to stimulate interest in utilizing the growing availability of waste salts for purposes that presently are of little financial significance to the world salt industry.

The Salton Sea is a source of low cost salts to meet the growing need for optimizing soil productivity and the parallel need for more and better rural roads at reduced costs.

## References

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## Appendix

G. J. Grott, Method of Reforming Soluble Salts to Effect Purification and Increase Crystal Size Thereof, U S Patent 5,300,123, (1994), Crude salt is ground in a manner to give maximum deformation of the small salt particles. Calcium sulfate and insolubles grind finer than the salt and most are removed during closed circuit grinding. Most of the calcium sulfate is removed with the insolubles and the dissolved calcium sulfate is largely removed by dewatering the ground salt before crystal reforming.

The grinding and deformation of the salt crystals increases their internal energy to the extent that the distorted salt particles will dissolve in an a solution already saturated according to conventional standards. The solution becomes locally supersaturated and the atoms reform into new material of normal lattice structure without evaporation. Agitation limits the incorporation of insolubles into the new crystals.

Typically, 200-500 of the small salt particles dissolve and reform as one crystal. The chemical purity is controlled by bleed-off through a side stream. The insolubles are separated by size.

Solar salt is easily purified to (Ca+ Mg) 4-7PPM and SO<sub>4</sub> to 10-20 PPM at 25-35 KWH/mt for the grinding process.

Mined salt with high calcium sulfate, clays, and fine inclusions take up to 65 KWH/ton.