

Washing of Solar Evaporated Salts

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ABSTRACT

The first stages of solar evaporation of Searles Lake brine deposit relatively pure sodium chloride. The sodium chloride harvest, however, is liable to be contaminated with salts deposited at the later evaporative stages, namely, burkeite ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$) and trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). It is possible to upgrade the sodium chloride to a 99+-% purity by screening and washing it with a suitable brine. A study of the Na_2CO_3 , Na_2SO_4 , Na_2Cl_2 phase diagram indicated the necessary information about the nature of the wash solution, the maximum impurities allowed in the contaminated sodium chloride, the ratio wash liquor/impure solids, and the final composition of the liquor after the washing step. Actual production experience produced a sodium chloride with carbonate and sulfate partially removed by a simple once-pass screening step. A final washing step in a continuous salt washer produced the finished product salt. Generally, salt quality was improved from 96% NaCl to 99+-% by the screening and washing processes.

INTRODUCTION

Searles Lake is a dry lake bed extending over an area of approximately 34 square miles (88 km²). It is an evaporative deposit formed in the last glacial age and contains salts deposited as a partial terminus of the water-flow from the nearby Sierra Nevadas into the Death Valley. The lake is located approximately 150 miles (240 km) north of Los Angeles. The evaporate deposit contains complex salts including carbonates, sulfates and borates. Sodium chloride production has only been a secondary activity at the lake whereas the more valuable constituents have been produced for the last 50 years. However, even though sodium chloride is a by-product, it is desirable to mine this particular constituent from the brine. Techniques, however, had to be developed to produce it from

the complex Searles Lake brines. This paper describes the experience of Searles Lake Chemical Corporation, a subsidiary of Occidental Petroleum Corporation, in solar salt production.

POND OPERATIONS AND HARVEST

Review of the solar salt producing facilities at Searles Lake is necessary in order to understand the selection of the various harvesting and salt processing technology. Basically, the brine is pumped from the sub-surface ore body into large solar ponds, and at the appropriate concentration, the brine is transferred to other ponds. Such a transfer in the processing scheme is to obtain the valuable salts that are available within the brine for production of borax, potash and soda ash. However, in order to get the brine to a concentration where these values will precipitate from solution, it is necessary to use preconcentration ponds where the sodium chloride is deposited from solution. The subsequent harvesting and salt washing activities were developed for the specific use on this type of deposit salt.

Pond production techniques. The Searles Lake ore body is an evaporative salt deposit with water in the interstices of the ore body. This saturated brine contains sodium, potassium, carbonate, sulfate, chloride and borate ions in the greater percentages. Other minor chemicals are also in solution. To show the complexity of the brine, a typical brine analysis as found by the U.S. Geological Survey (USGS) is shown in Table I. This brine which is high in the borate values as well as the sulfate values, is not as concentrated in the chloride values as is seawater or other solar salt producing brines. Therefore, since the brine is so complex, the proper timing in precipitating sodium chloride from solution is essential.

The brine is pumped from wells and put into a large solar evaporation pond (Fig. 1). The residence time in this

TABLE I

Composition of Searles Lake brine—upper body

	%
Na	10.9
K	1.93
As CO_3 total carbonate	2.39
SO_4	5.12
Cl	12.26
B_4O_7	.96
Specific gravity	1.285
Total dissolved solids (by summation)	33.6
pH	9.24

Reference—(Subsurface stratigraphy and composition of saline bodies, Searles Lake, California: A preliminary report, G. L. Smith, Open File Report 1973, U.S.G.S., Table 14.)

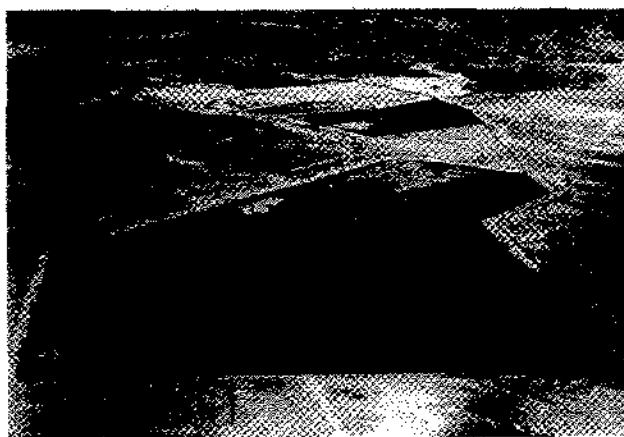


Figure 1. Large solar evaporation pond.

pond is limited in order to prevent the deposition of the valuable salts. The first non NaCl salt encountered would be burkeite ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$). Experience has shown that attention to the concentration factor, i.e., the ratio of the brine weight at any stage to weight of the original brine, should be maintained below 1.2 to 1.4 at a maximum. Such an operation therefore requires close monitoring because above the approximate value of 1.2 to 1.4, burkeite deposition begins.

The approximate period of solar pond activities is between May 1 and October 1. Earlier operations or later operations will result in the deposition of Glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Once the required concentration factor is obtained, the brine is continually transferred from the pond to other ponds where the more valuable constituents are recovered. When the evaporative season is over, the pond is drained to dryness in order to commence the harvesting operations. It is possible to harvest the sodium chloride while deposition is occurring; however, the draining of the pond at the end of the evaporative season is most important in order to prevent the production of Glauber salt.

It has been observed that as the concentrated brine is recovered from the solar ponds, pockets of brine are left as well as brine locked in the interstices of the deposited salts. This brine, being close to the critical concentration factor eventually evaporates to dryness. In so doing, it deposits the contained salts within the sodium chloride. Primarily, these contained salts consist of soda ash and sodium sulfate in the form of burkeite. The percentages of this contamination is dependent upon the proper timing of the transfer of the brine.

Harvesting. Once the pond is drained to dryness or semi-dryness, the harvesting operation commences. In the simple form, a blade grader is used to rip the thickness of deposited salt and windrow it for easy pickup by a front end loader as in Figure 2. It has been observed that this type of operation is extremely satisfactory in maintaining the integrity of the salt floor which is essential for future salt production. This harvest technique can be accomplished by using standard solid materials handling equipment. However, this harvesting technique was also undertaken because of the peculiarity of the harvest salt.

Salt deposition peculiarity. Close inspection of the deposited sodium chloride shows that it is deposited in a stratified layer. Of course, this can be related to the daily solar energy which is available. The crystals of the salt are of medium size, generally in the size of about 1/16 (15 mm) of an inch to 1/8 (31 mm) of an inch. Close inspection indicates that the deposition of the burkeite is localized within the particular salt mass. The burkeite seems to form a salt cluster with the sodium chloride in a localized random pattern. It has been observed that in the salt layer breakup and moderate handling of this particular salt, the burkeite acting as a bonding agent to the sodium chloride forms larger salt particles with high burkeite concentration areas. As we later were able to ascertain, this property was helpful in the improving of the salt quality through the use of screening prior to the washing step. In general,

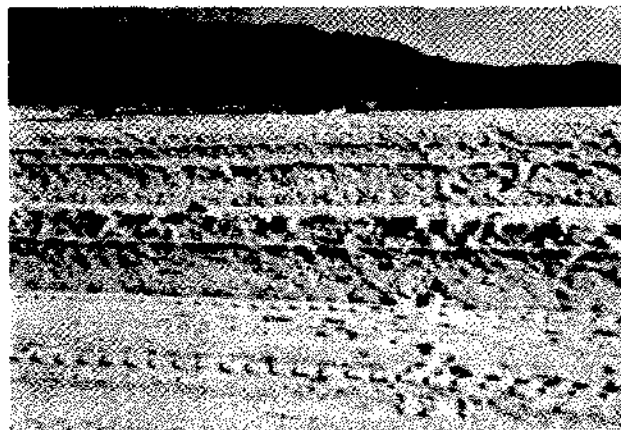


Figure 2. Windrowing of solar salt.

the salt harvested from the ponds was found to contain approximately an average of 93+% by weight of sodium chloride, the rest burkeite, thermonatrite, and possibly some trona, as shown in Table II. It was also observed that most of the burkeite clusters were in a size fraction of a +3/8 inch mesh. Further work indicated that harvested salts contained about 10% by weight of +3/8 inch (63 mm) mesh fraction.

PHASE CHEMISTRY OF THE WASHING PROCESS

As discussed, the crystallized sodium chloride contained minor amounts of the solids that are deposited in the second stage evaporation, i.e., burkeite, thermonatrite, and possibly some trona. Using some simple phase chemistry rules, the possibility of removing those impurities was examined by a selective washing either with water alone or with a suitable brine (obtained by making a 25% solution of the raw material) to arrive to a purity of 99+%.

Graphical and calculation approach. Although harvest sodium chloride proved to be more pure than tested, laboratory tests were conducted upon an assumed impure NaCl to determine the possible extremes in operations. Starting with an impure NaCl (7% sulfate and carbonate) it was determined in the laboratory that it is possible to upgrade salt to 99+% purity by washing with a brine prepared by dissolving one part of raw salt into three parts of water and using equal weights of impure salt and washing solutions. The operation would have to be done in a vessel equipped with agitation means but a two-stage lixivation was preferable. Contact time of each stage would be fifteen to twenty minutes.

The characteristics of the harvested sodium chloride were shown in Table II. The temperature of the experiments was chosen to be 20°C, since it was near the temperature of the brackish water available at the site, and because the conditions are slightly more favorable than at 30° or 35°C.

Figure 3 shows the phase diagram of the system Na_2Cl_2 , Na_2SO_4 , Na_2CO_3 at 20°C. The composition of the selected salt is represented by point M. If water is added, mixed with the feed salts in order to obtain a successful washing, the end solid must have the composition of point A (pure NaCl). The composition of the best possible end liquor will be found on the intersection of the extended line AM with PG (point N). The coordinates of this point, on the phase diagram, show only the molar composition percentage in relation to each other constituent. By a simple graphic calculation, and on basis of the position of Point N on line PG, it is easy to obtain the composition of N in moles per 1000 moles of water (see appendix). This calculation showed that point N would yield a brine of the following composition: Na_2Cl_2 45.4 moles, Na_2SO_4 13.6 moles, Na_2CO_3 8.85 moles (total moles 67.85), H_2O 1000 moles or, translated into ions percent: Cl^- 12.25%, SO_4^{2-} 5.0%, CO_3^{2-} 2.0%. This is an ideal end liquor where the figures for SO_4^{2-} and CO_3^{2-} are at their maximum for a yield of pure NaCl in preparation for further evaporation later. Practically, as it will be seen later, the values of sulfates and carbonates are lower while NaCl is higher.

A graphic determination also gave the theoretical ratio of water to be used per unit of feed salt: 4:1% (see appen-

TABLE II

Harvested salt composition

A. In % of solid phases:

93%	Halite	(NaCl)
6%	Burkeite	($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$)
1%	Trona	($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$)

B. In % of constituents:

(Neglecting the small amount of NaHCO_3 and H_2O)

93.5%	NaCl
4.4%	Na_2SO_4
2.1%	Na_2CO_3

C. In ions %:

Cl	=	56.55
SO_4	=	2.98
CO_3	=	1.15

D. In moles per 100 gpm:

Na_2Cl_2	=	0.800
Na_2SO_4	=	0.031
Na_2CO_3	=	0.020

E. In moles % in respect to each other constituent:

Na_2Cl_2	=	94.0
Na_2SO_4	=	3.65
Na_2CO_3	=	2.35

On the Phase diagram of Figure 3, the salt is represented by Point M.

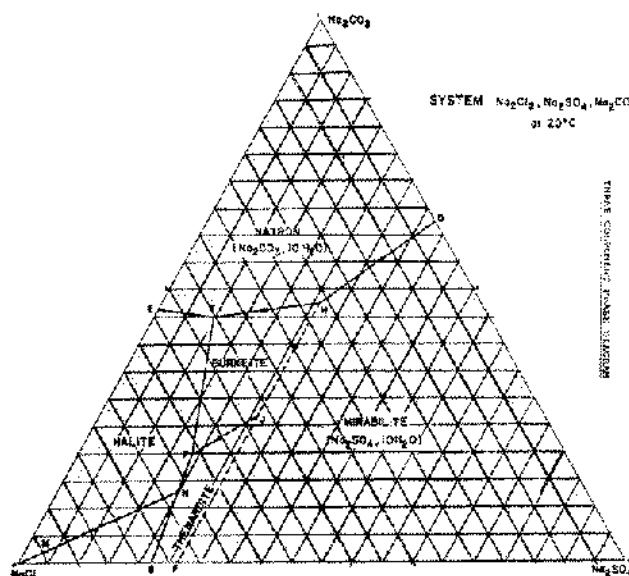


Figure 3. Three component phase diagram.

dix). Figure 4 shows the calculated material balance for a water wash, and it was seen that the ratio of water used was 41%.

Experimentation. The composition of the end liquor and the subsequent weight ratios R (water/solid) or R' (washing solution/solid) were assumed to be equilibrium conditions necessitating a very long residence time. In practice, a faster washing is mandatory and therefore the R or R' were assumed to be increased. A good figure for R' was chosen to be $R' = 1$. While in this case the residence time is shorter, it was expected that the values for SO_4^{--} and CO_3^{--} would be lower than the equilibrium figures (point N) and NaCl will be higher. With the level of impurities in the raw salts, agitation was anticipated as a necessity to perform a successful washing. All other means of contacting (percolation, etc.) gave poor lab results. Furthermore, a two-stage operation was found to yield a better purity of the washed solid. Figure 5 shows the details of a two-stage experiment where the final solid obtained was 99+% NaCl.

As actual operations showed, this washing technique could be simplified if the raw salt has a purity level of 97 to 98%.

SCREENING TO IMPROVE WASHING RESULTS

As the previous discussion on the phase chemistry of the salts at Searles Lake indicated, extensive washing would be necessary if the raw harvest salts were to be taken directly into the washing scheme. The review of a possible physical beneficiation technique on the sodium chloride prior to washing was made.

Test screens. From our earlier reviews, it appeared as though the sulfate and carbonate contents were contained mostly in the +3/8 inch (63 mm) mesh of the screening

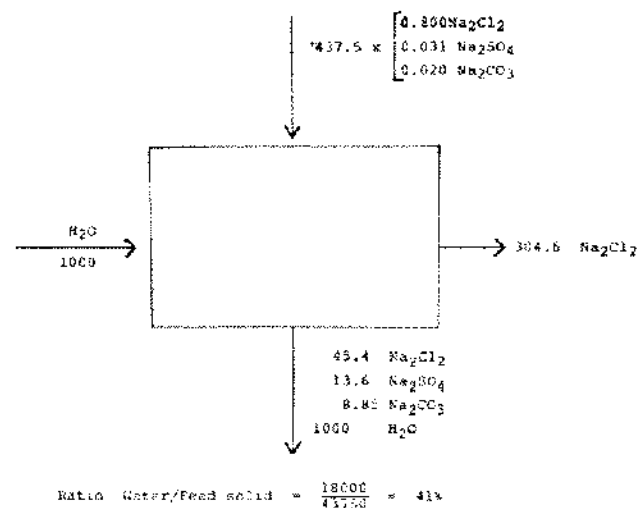
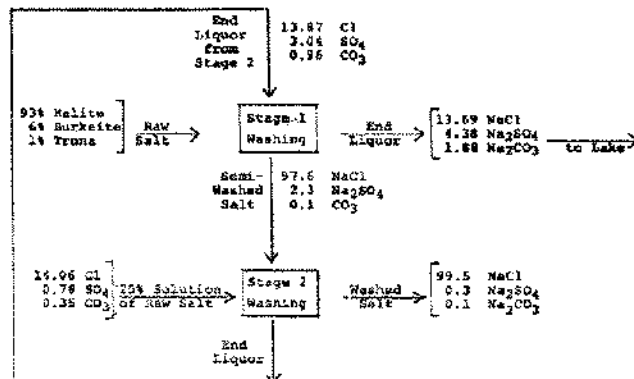


Figure 4. Feed salt washed with water at 20°C—calculated water wash.



The figures for the solid phases are shown entrainment free.

Figure 5. Calculated two stage water wash.

operation. Since it appears that the screening could remove most of the sulfate and carbonate content of the salt, it was decided that if one adopted the screen separation before a salt washing system that quality sodium chloride could be produced with minimal washing.

Harvested salts contained about 5 to 10% by weight of +3/8 inch (93 mm) mesh material. The +3/8 inch mesh fraction analyzed as 85% chlorides, 16% burkeite, and 1% trona. The below 3/8 inch mesh fraction analyzed as 98% chloride, 1% burkeite, and 1% trona. It was also observed that the sulfate and carbonate content of the salt increased with increasing particle size. The -1/2 inch +3/8 inch (-125 to +93 mm) fraction had 16% burkeite, and -1 inch +1/2 inch (-250 to +125 mm) had 24% burkeite. This reaffirms our earlier observations that the burkeite or the carbonate sulfate portions act as a bonding agent to form larger particles. Subsequent investigations of the various salt samples by screening indicated that the purity of the salt at various locations changed much where there were pockets of brine remaining after the pond was drained. In these pockets the burkeite concentration would be much higher. However, since it was difficult to differentiate where these pockets would occur it was felt necessary to screen the whole salt harvest. As a matter of fact, it is shown (Table III) that the unscreened salt was 96.8% sodium chloride and that subsequent screening produced a much higher purity sodium chloride, approaching the quality desired, 99+%. When this result is

TABLE III

Characteristic of harvest salt

Sample Description	Feed Salt Weight %		
	NaCl	SO ₄	CO ₃
Unscreened Salt	96.8	0.96	0.69
-3/8" + 1/4" Salt*	97.6	0.81	0.63
-1/4" Salt**	98.5	0.25	0.54

*3/8" = 93 mm

**1/4" = 63 mm

compared to the earlier feed salts it indicates that the variability of salt quality through the salt harvest was in fact apparent.

Final screening operation. A movable screen was positioned on the pond site, and a front end loader would pick up the windrowed salt and feed it to the screen. The screen sized the harvest salts through a 3/8 inch (93 mm) mesh with the oversized fraction being separately stockpiled from the undersized. The oversized fraction eventually was taken from the site and dumped into disposal beds. The undersized fraction represented the purer quality salt and was subsequently passed through the washing plant for further removal of the carbonate and sulfate contaminants. Analysis of samples of the undersize and oversized fractions, devoid of the larger +1 inch (250 mm) chunks, found essentially the same 98+% sodium chloride. However, after testing a large 5/8 inch (1.5 mm) mesh screen during operations, the quality of the salt obtained by the insertion of this screen was found not to be as desirable for entrance into the washing plant.

WASHING SALT FOR PRODUCT IMPROVEMENT

As shown earlier, theoretical calculations from the laboratory indicated that to get 99% sodium chloride from a thorough washing would require 50 tons of water for 100 tons of pure salt. This approach would give the process approximately 86% yield on sodium chloride or 81% on a net weight basis. Brines saturated with sodium chloride, burkeite, and thermonatrite would have a theoretical sulfate and carbonate content of 4.8 and 3.2% by weight respectively. In actual practice a saturated brine of 4% sulfate and 1.6% carbonate levels as encountered in the brine in about 10 minutes of equilibrium.

As a test on the available washing facility, three runs were made at a set fee and rate and varying the water rates. Each experiment was run for one hour. Table No. IV shows the actual water to salt weight ratios with the particular salt analysis and brine analysis for the various schemes adopted. The ultimate level of washing then was at 0.28 parts of water per part of harvested salt. The combination, therefore, of a 3/8 inch (93 mm) mesh screen and washing the undersized fraction with 0.14 to 0.28 parts of water per part harvested salt yielded a 99+% sodium chloride. The screening losses will vary on a daily basis from 5% to 10% by weight at the pond. The washing losses are approximately 8%.

The washing facilities

Figure 9 attached, gives the principal sizes and dimensions of the washing facility. Basically, a 6 inch (21 cm) grizzly leading into a feed hopper and subsequently to a 60 ft (18.6 m) transfer belt, brings the salt to the mill and initial wash contact point. At this point, an 18 ft (5.6 m)

TABLE IV
Typical chemical analysis of various streams

1. Water to salt weight ratios	28/100	56/100	14/100
2. Feed salt analysis (moisture free)			
%NaCl	97.5	97.5	97.5
%Burkeite (%SO ₄)	1.36	1.36 (0.65)	1.36 (0.65)
%Na ₂ CO ₃ (%CO ₃)	1.06 (0.68)	1.06 (0.68)	1.06 (0.68)
3. Washed salt: (moisture free)			
%NaCl	99.03	99.1	98.58
%Burkeite (%SO ₄)	0.47 (0.23)	0.43 (0.21)	1.04 (0.51)
%Na ₂ CO ₃ (%CO ₃)	0.50 (0.36)	0.47 (0.33)	0.38 (0.42)
4. Brine analysis:			
% dissolved solids total	26	25	25
%SO ₄	0.59	0.64	1.10
%CO ₃	0.8	0.71	1.14

classifier of 38 inch (1 m) diameter, moves the sodium chloride up a 16° incline. The counter current waterflow washes the sodium chloride for approximately a 10 minute residence time. A pivoting stacker deposits the salt on the drying and storage stacks.

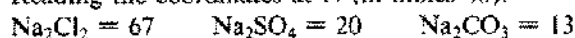
SUMMARY

The production of solar salt at Searles Lake is possible although the source of sodium chloride is a complex brine. Proper movement of brine at the designated intervals will give the harvested salt a purity which would be desirable to take to the wash plant. The peculiarity of the brine causes the impurities to be located in screenable particles. Subsequent washing will improve the final product to 99+% level with relative simple screening and washing techniques. A high quality sodium chloride can be produced from the complex Searles Lake brine.

APPENDIX A CALCULATIONS

I. Composition of the brine at Point N

Reading the coordinates at N (in moles %):



P has a total moles composition of 71.3 per 1000 moles H₂O

(Data in Figure 1).

G has a total moles composition of 62.9 per 1000 moles H₂O

(Data in Figure 1).

The difference is 8.4 representing the total section PG.

If X is the difference at Point N, then NP/PG = X/8.4 measuring MP and PG, X/8.4 = 6.8/19.8 where X = 3.45. Therefore, the total moles at N will

be $71.3 - 3.45 = 67.85$ per 1000 H_2O . The molar composition at N will then be:

$Na_2Cl_2 = 0.67 \times 67.85 = 45.4$	or in ions %
$Na_2SO_4 = 0.20 \times 67.85 = 13.6$	Cl = 12.25
$Na_2CO_3 = 0.13 \times 67.85 = 8.8$	$SO_4 = 5.0$
$H_2O = 1000$	$CO_3 = 2.0$

II. Graphic calculation of the water to be used

$$\frac{AM}{MN} =$$

$$\frac{6}{27} =$$

Total moles of solute in liquid phase

Total moles in solid phase

If W is the water corresponding to the total moles in the liquid phase, then: $6/W = 67.85/1000$ (Point N)

where $W = 88.5$ Moles = 1590 gm

The original salt were before washing = $6 + 27 = 33$ moles if 0.851 moles (See Table I) represent 100 gm then 33 moles will represent $33 \times 1000/0.851 = 3880$ gm

Ratio R water/feed salt = $1590/3880 = 41\%$

This figure is the same as the number calculated in Table II.