

Recovery of Lithium From Saline Brines Using Solar Evaporation

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ABSTRACT

The Foote Mineral Company is recovering lithium from solar evaporated saline brines at Silver Peak, Nevada. The brines are pumped from beneath a playa surface inside a closed basin. The playa deposits consists of mixtures of clays, silts, sands, and evaporites, many of which are saturated with saline brines down to known depths of 600 feet. Brines are probably present below this depth, for gravity studies have indicated the unconsolidated sediments reach depths of 1500 feet. The genesis of the Silver Peak deposit is apparently related to volcanic activity and the area is characterized by hot springs, cinder cones, and lava deposits. The brine pumped from wells contains 300 ppm of lithium and 10-15 wt. % of other dissolved solids. The playa surface is well suited for solar evaporation. The brines are pumped into a series of solar evaporation ponds and after they reach saturation a series of salts are precipitated. The sequence of salts precipitated is NaCl, a mixture of NaCl and glaserite ($K_3Na(SO_4)_2$), and then these two plus KCl. As a consequence of the evaporation, the lithium concentration is increased to approximately 5000 ppm. The effective evaporation season at Silver Peak begins in April and commonly continues through October. It is necessary to accumulate sufficient brine by October to operate the processing plant through the winter months. Lithium is recovered from the brine by precipitating lithium carbonate.

GEOLOGY AND HYDROLOGY

The Silver Peak playa, occupies the lowest part of Clayton Valley in Esmeralda County, Nevada,

within 20 miles of the California border. The playa is elongated in a general northeast-southwest direction, measuring about ten miles in length and about four miles in maximum width. Its area is about 32 square miles. Clayton Valley is located physiographically within the Basin and Range Province as defined by Fenneman (1931). The Basin and Range Province consists of block mountains largely buried in their own debris. The ranges are uplifted and tilted blocks consisting mainly of Precambrian and Paleozoic rocks or of Cenozoic volcanics. The low areas between the ranges originated as down-dropped blocks created basins which filled with Miocene, Pliocene, Pleistocene nonmarine deposits, and in part with Recent alluvium.

Clayton Valley includes a mountainous border, a playa, and alluvial slopes that extend from the mountains down to the playa. It is an enclosed basin with internal drainage, typical of many similar basins in southwestern Nevada.

The mountains and ridges surrounding Clayton Valley are underlain by rocks that range in age from the Precambrian to Tertiary. The oldest rocks consist mainly of limestones, dolomites, siltstones, slates, shales and quartzites. Tectonic forces, some associated with Mesozoic intrusives, have folded, faulted and metamorphosed them to some extent. Volcanics and sediments of Tertiary age are also present in the ridges. The main types of volcanics are tuffs and ash flows. The materials on the alluvial slopes are predominantly unconsolidated to semi-consolidated sands and gravels that have been derived from the rocks in the bordering mountains and ridges.

The sediments underlying the playa are of particular interest because some of them contain the

high lithium-bearing brines. Drilling has indicated that they are essentially flat-lying and that facies changes do occur laterally. In the immediate area of the present production field, clays and silts predominate with the remaining deposits of fine sand, or gypsum.

The playa, sometimes referred to as the Silver Peak Marsh, is at an elevation of about 4270 feet. The surface is usually dry and covered for the most part with a white crust of sodium chloride, except after periods of heavy precipitation when run-off forms a pond upon the clays in the low part of the playa. Laterally, the clays grade into coarser materials at the margins of the playa and eventually into the coarser alluvium found on the slopes of the valley.

The climate is distinctly arid. The evaporation rate is high, averaging more than 50 inches per year. More than 75 percent of the evaporation occurs during the months of April through October. Annual precipitation does not exceed six inches per year. The drainage area, however, is about 520 square miles so that the total precipitation in the basin probably exceeds 150,000 acre-feet per year. Evapotranspiration returns much of the total precipitation back to the atmosphere. Rush (1968) estimates evapotranspiration from the playa to be 24,000 acre-feet per year. His preliminary ground water budget indicates that the recharge rate from subsurface inflow is 20,000 acre-feet. Some recharge is due to precipitation (1500 acre-feet).

BRINE PRODUCTION FIELD

The brine production field is located on the west-central part of the playa. It extends over an area of about two square miles. Thirty production wells have been drilled into the sediments underlying the playa. The wells range from 300 to 700 feet deep. The wells consist of a 12 inch perforated casing for the full depth, surrounded by about six inches of gravel packing. Brine is pumped by means of a multi-stage centrifugal pump set at the bottom of the well. Brine from the wells is transferred by pipe lines to a 760 acre pond which is the first in a series of nine solar evaporation ponds.

SOLAR EVAPORATION PONDS

The composition of a typical well brine is given in the following table. The well brine contains approximately 16 weight percent dissolved solids, most of which is NaCl. This brine does not reach saturation until the dissolved solids reach 31 per-

cent and the lithium concentration has increased to about 600 ppm. Further evaporation is accompanied by the precipitation of NaCl and other salts.

Table 1. Silver Peak Brines

	Well Brine Wt. %	Rich Brine Wt. %
Na	6.2	7.8
K	0.8	4.8
Mg	0.04	0.007
Li	0.04	0.50
Ca	0.05	0.004
SO ₄	0.71	2.9
Cl	10.1	16.1

The lithium concentration of the final rich brine is 5000 ppm. This is a twelve-fold increase over the well brine concentration and an eight-fold increase over the point at which the brine initially becomes saturated. This means that for each 100 pounds of well brine, 78 pounds of water are removed by solar evaporation and 13.5 pounds of salts are precipitated to produce eight pounds of final rich brine containing 0.04 lbs. of lithium. The precipitated salt is mainly NaCl. The precipitates contain voids which are filled with brine. This brine, "trapped brine," represents a loss of lithium.

This loss can be calculated for the special case of batch evaporation of saturated brine in a non-leaking pond:

- C = Li concentration at the end of a given time period.
- C_i = Initial Li concentration.
- V_i = Initial brine volume.
- E = Volume of brine disappearing due to evaporation during the time period (same units as V_i).
- T = Volume of brine trapped in the precipitated salt.
- $T/E = K$ (K is a constant for a given brine system and evaporation condition. The K for the Silver Peak evaporation ponds is 0.11 ± 0.02). (1)

The lithium concentration is equal to the quantity of lithium divided by the volume of brine.

$$C = \frac{C_i V_i}{V_i - E} \quad (2)$$

$$\frac{C}{C_i} = \frac{C T}{C_i V_i} = \frac{1}{K} = 1$$

The fraction of lithium lost is equal to $\frac{C T}{C_i V_i} = K \left[\frac{C}{C_i} - 1 \right]$.

The loss of lithium depends upon the ratio of final lithium concentration to the initial concentration. For example: at a concentration ratio of five, for K value of 0.11, the loss of lithium is 0.44. The loss becomes 0.80 at a concentration ratio of eight.

The constant K (ratio of volume of trapped brine to the evaporation volume) is determined from the void fraction of precipitated salt (F), the density of brine (D_b), the true crystal density of precipitated salt (D_s), and the weight fraction of dissolved solids in the brine (W).

$$K = \frac{F}{1-F} \cdot \frac{D_b}{D_s} W.$$

In order to achieve an overall lithium enrichment of greater than ten with an average K value of about 0.10, it is necessary to use a series of solar evaporation ponds. This minimizes the lithium lost due to trapped brine because a low lithium concentration ratio can be used in each pond. Obviously, the maximum yield would be achieved with an infinite number of ponds. From a practical standpoint, a series of nine ponds gives a satisfactory overall lithium yield.

The general equations for a solar evaporating pond operating in series with other ponds are given below. A pond has:

- Brine input rate (I) at the lithium concentration of the pond feeding it (C^*).
- Brine output rate (O).
- Brine evaporation rate (E).
- Brine leakage rate (L).
- Brine trapped (T).
- Lithium concentration (C).
- Brine volume (V), the volume of brine not counting trapped brine.
- Quantity of lithium in the brine (Q), not counting trapped brine.
- $Q = CV.$ (3)

The differential change in volume is:

$$dV = dI - dO - dE - dT - dL. \quad (4)$$

The differential change in quantity of lithium in the pond is:

$$dQ = C^* dI - C dO - C dL - d(CT) \quad (5)$$

$$dQ = C^* dI - K dC - C(dO + dL + K dE).$$

These two equations (4 and 5) can be written for each pond in a series, multipond system. A mathematical solution can be obtained, either by integral methods or by use of small time increments. From the solution, one can obtain the total yield of lithium, the amount lost in each pond, and the optimum areas and operating depths for each pond for any amount of evaporation.

The final pond, used for accumulation of rich brine is a special case, since its concentration is to be held constant at a predetermined value. Assuming that it does not leak, its input is

$$I = \frac{C E}{C - C^*}$$

where C^* , as before, is the concentration of the brine fed to the final pond.

We have found it necessary to program a high-speed computer to solve these equations. Data inputs to the computer are the measured lithium concentration, the measured brine volume, salt volume, salt void fraction, expected evaporation, pond area, pond leak rates, and the brine input to the pond system from the brine wells.

The determination of leak rate cannot easily be separated from the evaporation rate. Daily evaporation is measured in a ten foot diameter pan by methods similar to those described by the Weather Bureau for Class A pans. This can be correlated with actual evaporation on the large solar evaporation ponds. The evaporation and leakage from a solar evaporation pond is estimated by making a careful brine and lithium balance over a short time period (minimum of one week). The brine disappears from a pond due to both evaporation and leakage, while lithium losses are due entirely to leakage.

A typical set of lithium concentrations and brine volumes is given in the table on the following page for a time early in the evaporation season.

Well brine is pumped into pond No. 1. The brine flows through the ponds to the final storage pond (No. 9). Slaked lime is added to the brine pumped from pond No. 4, which raises the pH to about 11. The lime addition removes most of the magnesium

Table 2. Silver Peak Pond System. Typical Data.

Pond No.	Area (Acres)	Brine Vol. (Thous. Gallons)	Li Conc. (ppm)	Solid Phases
1	760	200,000	680	None
2	520	120,000	780	NaCl
3	90	25,000	930	NaCl
4	86	22,000	1200	NaCl
5	46	15,000	1400	NaCl, gypsum, $Mg(OH)_2$
6	41	5,500	1900	NaCl, $CaCO_3$
7	17	1,500	2400	NaCl, Glaserite
8	13	1,000	3100	NaCl, Glaserite, KCl
9	14	3,000	5000	NaCl, Glaserite, KCl

and reduces the sulfate content of the brine. The gypsum and hydrated magnesia precipitate in the next pond (No. 5). Most of the calcium precipitates in the subsequent ponds due to absorption of CO_2 . Glaserite ($K_2Na(SO_4)_2$) starts to precipitate when the brine reaches a lithium concentration of about 2000 ppm.

Strong brine from the storage pond is pumped to the lithium carbonate processing building. After treatment to remove minor amounts of magnesium and calcium, lithium carbonate is precipitated by mixing with a solution of sodium carbonate. The lithium carbonate is washed on a belt filter, dried, and packaged.

At present, the Silver Peak brines with the solar evaporation ponds and processing plant contribute more than 25 percent of the domestic supply of lithium. Other sources are the brines of Searles

Lake, California, and the spodumene deposits in North Carolina.

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