# Production of Bischofite from Leaching Effluent by Solar Evaporation

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*ABSTRACT*

*Titanium Metals Corporation of America uses a leaching process in the production of titanium metal sponge. The spent leaching effluent contains magnesium chloride in solution.*

*A process has been developed to use solar evaporation ponds to produce bischofite, $MgCl_2 \cdot 6H_2O$, from this effluent.*

*Uses for the products from the solar evaporation ponds are being developed. The first successful product marketed was the concentrated brine itself, for use as a dust control agent on dirt roads.*

*Other possible applications include the use of the brine in solar ponds for thermal energy or electrical energy production, using the bischofite as a feed material in the manufacture of periclase and hydrochloric acid, or using the magnesium chloride to make oxychloride cements.*

*Information on pond construction, lining material, pond chemistry and temperature cycles will be included.*

## INTRODUCTION

In the production of titanium metal (titanium sponge) by the modified Kroll process, Titanium Metals Corporation of America (Henderson, Nevada) generates a leaching effluent that is high in magnesium chloride. As generated, this leach liquor contains about 17% magnesium chloride and 2½% magnesium nitrate, and is collected in lined ponds.

### Evaporation Rates

Prior to designing the first ponds, solar evaporation tests were run on the leach liquor and the evaporation rate was compared to the normal evaporation rate of water. The annual evaporation rate for water in southern Nevada was found to be about 83 inches per year, with the summertime months as high as 15 inches per month. The evaporation rate of the magnesium chloride-containing leach liquor was much less than water, as would be expected, and it was discovered that the evaporation rate decreased drastically as the solution became more concentrated. In fact, after a 50% decrease in volume, the evaporation rate dropped to zero and the brine solution remained in equilibrium with the atmospheric humidity. On this basis, our first series of leach liquor ponds were built 18 feet deep, in order to maximize storage volume. As these ponds were filled, the test data were confirmed. The brine about doubled in concentration by solar evaporation and then no further evaporation occurred.

It became readily apparent that adding ponds every year or two for storage of effluent would be necessary. These deep ponds were not only expensive to install but they were consuming large segments of real estate. It was obvious that a more economical approach to management of the magnesium chloride brine was needed.

## BISCHOFITE PROCESS DECREASES PONDING COSTS

Several processes were examined for ways of recovering products of economic value from the brine being accumulated in the ponds. These processes included spray drying to produce magnesium chloride powder, spray roasting to produce magnesium oxide and hydrochloric acid, and wet processes to produce magnesium carbonate or magnesium hydroxide by treatment with soda ash or lime. In all of these cases there were problems due to the large volume of water to be evaporated, or difficulty in achieving the required final product purity.

TIMET changed its pond design strategy from deep ponds, for maximum storage, to shallow ponds for maximum evaporation. The shallow ponds result in higher brine temperatures. The temperature range in southern Nevada is shown in Table 1 and Figure 1 shows brine temperatures achieved in our evaporating ponds in the summer of 1982. With the high temperature and low humidity that occur in southern Nevada in the summer, it was theoretically possible to obtain sufficient evaporation to

TABLE I

Southern Nevada climatological data

| Month | Extreme High °F | Normal High °F | Normal Low °F | Extreme Low °F | Normal Rainfall, Inches | $\bar{X}$ % Rel. Humidity | % of Poss. Sunshine |
|---|---|---|---|---|---|---|---|
| J | 77 | 56 | 33 | 8 | 0.45 | 44 | 76 |
| F | 82 | 61 | 37 | 18 | 0.30 | 38 | 81 |
| M | 91 | 68 | 42 | 23 | 0.33 | 32 | 83 |
| A | 98 | 78 | 50 | 31 | 0.27 | 24 | 86 |
| M | 109 | 88 | 59 | 40 | 0.10 | 22 | 88 |
| J | 115 | 97 | 67 | 49 | 0.09 | 17 | 92 |
| J | 116 | 104 | 75 | 62 | 0.44 | 21 | 87 |
| A | 116 | 102 | 73 | 56 | 0.49 | 24 | 88 |
| S | 113 | 95 | 65 | 46 | 0.27 | 24 | 92 |
| O | 103 | 81 | 53 | 26 | 0.22 | 28 | 86 |
| N | 85 | 66 | 41 | 21 | 0.43 | 36 | 81 |
| D | 77 | 57 | 34 | 15 | 0.37 | 43 | 78 |
| YR $\bar{X}$ | | 79 | 52 | | 3.76 | 29 | 85 |

Mean Wind Speed ~ 9.1 mph

produce magnesium chloride hexahydrate crystals (bischofite). However, it was necessary to add neutralization facilities in order to control the pH of the brine. A two-step neutralization process is used. About 50% of the neutralizing is achieved by flowing the leach liquor through a shallow lined pit that is partially filled with coarse dolomitic limestone. The final neutralization is accomplished with soda ash.

Schematically, the brine flow is illustrated on the flow sheet shown in Figure 2. The flow rate is controlled so that, by the time it reaches Pond 6A, the solution density has increased to about 1.35, and most of the sodium and ammonia are crystallized out of solution as $NH_4Cl$ and NaCl. Thus, the brine transferred out of Pond 6A contains primarily $MgCl_2$, $Mg(NO_3)$ and $CaCl_2$.

**Bischofite Production**

In 1982, the final series of shallow ponds, 7A, 7B and 7C, were added. These ponds are designed to be harvesting ponds because they are being used to produce solid crystals of bischofite ($MgCl_2 \cdot 6H_2O$). The bischofite forms in distinct individual acicular crystals, similar to jack straws. In the summer of 1982, we produced about a one-foot depth of these crystals in three five-acre ponds. However, the brine did not go completely to dryness. The crystals remained saturated with an invariant residual brine which would not go to dryness. The invariant brine is high in nitrate and calcium, with a typical composition of 23% $MgCl_2$, 15% $Mg(NO_3)_2$, 8% $CaCl_2$ and 1% NaCl. It is called "invariant" because the brine will not go to dryness as long as it remains mixed with the crystals.

Also, the bischofite crystals cannot be easily harvested from the ponds directly because of this brine. If the crystals are pumped, or picked up with a front-end loader, or handled mechanically in most any other way, the needle-like structure is broken and the crystals and brine produce a mush that flows together, much like slushy ice. In order to harvest the bischofite crystals, it is necessary to drain the invariant brine away from the crystals. Then the drained bischofite can be mechanically harvested as any dry salt. The crystals will remain firm and dry as long as the ambient humidity is low, i.e., less than about 35%.

At the time this paper was written, only token amounts of bischofite crystals had been harvested from the large quantity produced. Testing was underway, however, to cut furrows, or windrows, in the bischofite in Pond 7C in order to open up drainage channels for the invariant brine. We intend to pump the invariant brine into Pond 7B and then demonstrate a simple harvesting technique for the dry bischofite by using a front-end loader to stack it into a pile inside the pond. Samples of bischofite were stacked with a shovel and allowed to sit for 24 hours so that all the invariant brine drained away from the crystals. These raw bischofite crystals were analyzed and found to have a purity of 76.2% to 96.9% $MgCl_2$, calculated on an anhydrous basis. The average purity of 10 samples was

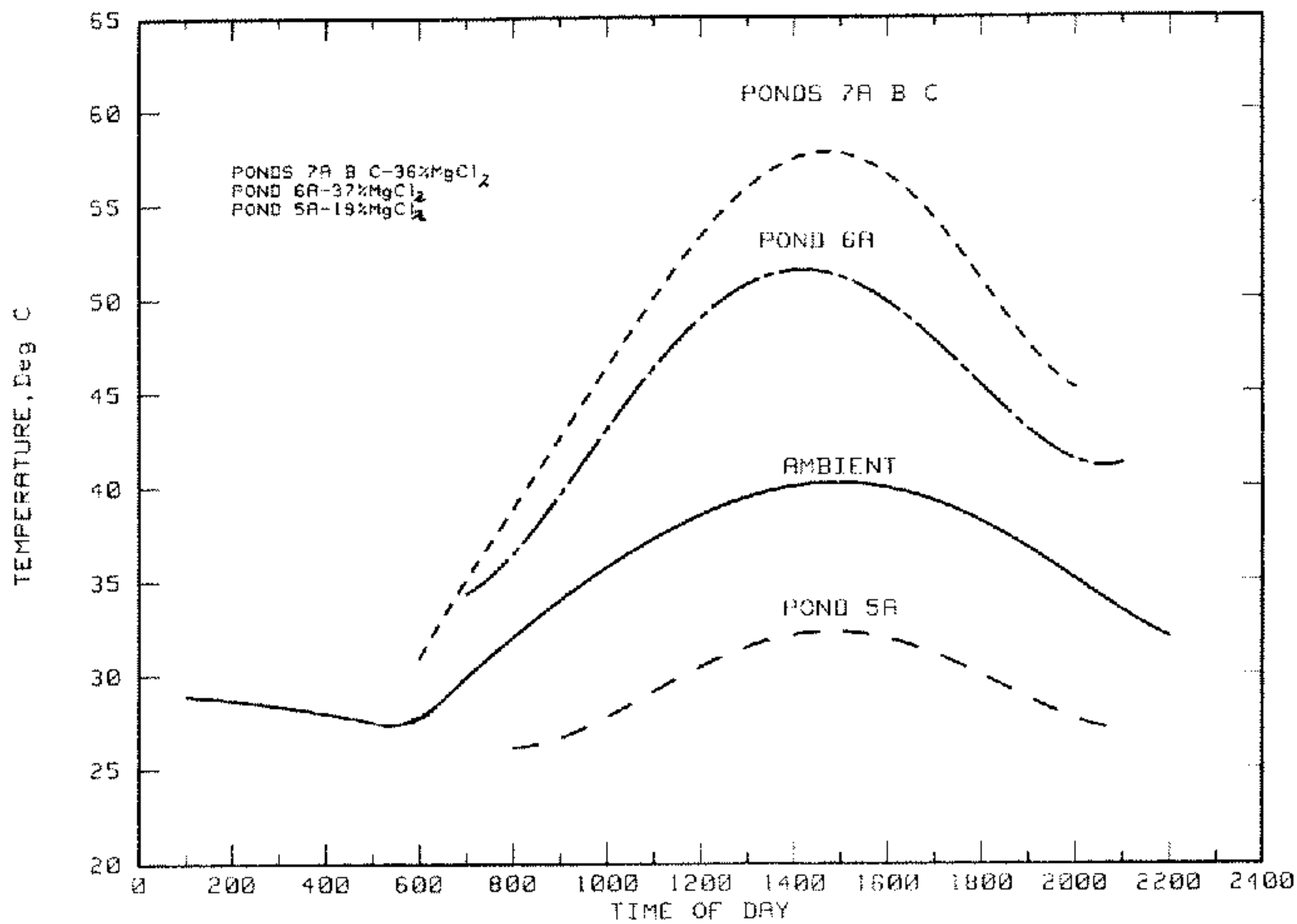


**Figure 1.** Brine and ambient temperatures-typical July day.

92.4%. The impurities were primarily $Ca^{2+}$, $Na^+$, $NO_3^-$, $NH_4^+$, and a trace of $SO_4^{2-}$ and $Fe^{2-}$.

**Washed Bischofite**

Laboratory washing of this raw bischofite was done to upgrade its quality. Samples of the raw crystals were washed with a saturated aqueous solution of $MgCl_2$. Three samples of washed crystals had an average analysis as follows, on an anhydrous basis: 98.63% $MgCl_2$, 1.25% $NaNO_3$, and 0.15% "other." The 0.15% "other" consisted of small amounts of $Ca^{2+}$, $NH_4^+$, $SO_4^{2-}$, $K^+$ and $Fe^{2+}$. It is presumed that a bischofite product of this purity would have commercial value, although none has been sold at this time. Bischofite can be used as a "feed stock" for producing spray-dried anhydrous $MgCl_2$ for electrolytic magnesium cells, or it can also be used for the production of high purity refractory-grade periclase (MgO) and hydrochloric acid by thermal decomposition.

**Proposed Treatment of Invariant Brine**

If the bischofite can be successfully harvested, the invariant brine would still remain. It has been proposed to manufacture a magnesium nitrate solution by treating the invariant brine with a solution of sodium carbonate. The carbonate will precipitate the calcium and by selective additions can be used to precipitate the magnesium portion of the magnesium chloride. Then, by controlling the brine concentration, the sodium chloride should crystallize out, leaving a brine that should be high in magnesium nitrate. Laboratory tests produced a brine concentrate of about 65% $Mg(NO_3)_2$ and 35% NaCl on an anhydrous basis. This proposed process is illustrated in Figure 3.

## BRINE USAGE FOR DUST CONTROL & SOIL STABILIZATION

At the same time as the bischofite process was being developed, other uses for the brine were being explored. As far back as 1977 the use of magnesium chloride brine as a dust control and soil stabilization agent had been proposed. Field testing showed excellent results and the first sales of leach liquor for treating roads were made in 1978. It wasn't, however, until 1982 that serious efforts were made to promote the brine for use on dirt roads. It has now

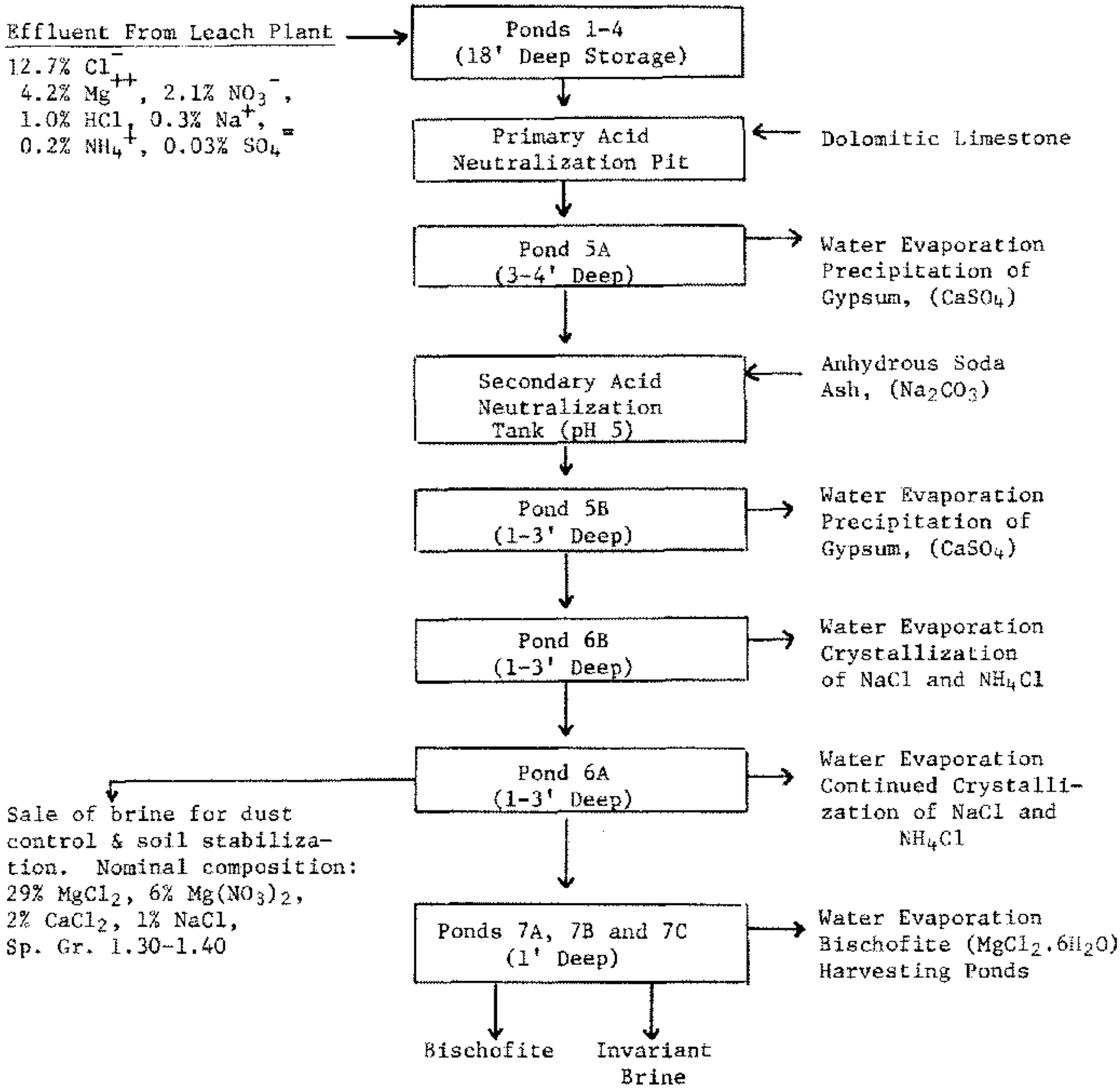


**Figure 2.** Brine flow sheet—present process.

become an acceptable road treatment product in the western parts of the USA, and about 25% of TIMET's brine generated in 1982 was sold for dust control and soil stabilization.

### History of Dust Control

The following historical data concerning the use of sodium chloride as both a dust palliative and stabilizing agent are quoted directly from the Salt Institute's publication, "Salt For Road Stabilization," revised edition dated 1975:

*The knowledge that the addition of salt stabilizes soil is not new. Writings of early centuries tell that when salt was spilled accidentally on an ancient Roman road that its surface became harder and chariot wheels raised less dust.*

*Not as many years ago the clay floors of horse stalls and vegetable cellars were salt treated to hard pack the surfaces. Another age-old practice was to salt the tread paths of work animals driven repeatedly over the same ground.*

*Salt as a low-cost ingredient in modern highway*

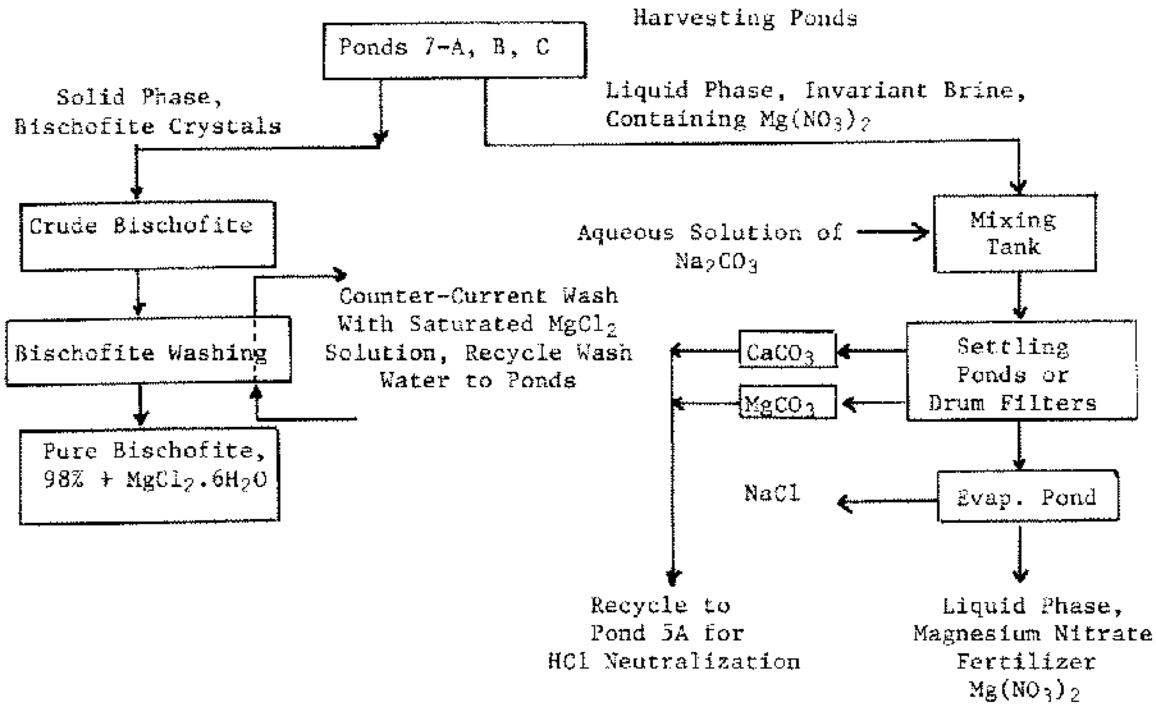


**Figure 3.** Proposed future processing flow sheet.

*building possibly traces to an American construction firm working in Greece in the 1920s. Building dirt roads to transport equipment from coastal ports to the construction site, the crews were confronted by a severe dust problem. They used sea water to stop the dust clouds. After repeated waterings, the roads no longer became dusty even when dry and had become stabilized with a hardened surface. Less grading maintenance was required.*

*Nova Scotia used the discovery for the first time in the Western Hemisphere with a salt stabilized road near Canada's first rock salt mine at Malagush. By 1932, a similar road had been built on Avery Island, Louisiana. This was followed by another near Ithaca, New York.*

*Study of various mixtures of salt and soil continued. By 1935, some 29 states had salt stabilized mileage and the test period was well underway. In the following years, road-builders' understanding of the principles and methods of salt stabilization had been developed to where road stabilization with salt had become a consistently predictable science.*

## Problems Resulting from Unpaved Roads

There are almost four million miles of roadways in the United States divided into these categories (Israel, 1982, p. 1):

| | |
|---|---|
| A. Portland Cement Concrete | 117,000 Miles |
| B. Bituminous Surfaces | 1,850,000 Miles |
| C. Gravel Surfaces | 1,200,000 Miles |
| D. Unsurfaced "Dirt Roads" | 700,000 Miles |

There are some interesting facts concerning these unpaved roads that result from studies at the Geo-Technical Research Laboratory of Iowa State University. Each mile of gravel-surfaced road produces one ton of dust per mile per year multiplied by the average daily traffic count. One hundred vehicles per day, 100 tons of dust per mile each year. Most of this is mineral dust resulting from degradation of aggregates and must be replaced at an enormous annual cost to taxpayers.

The cost of automobile maintenance is many times greater for each mile traveled over these roads, and there are 230% more fatal accidents for each mile traveled compared to travel on paved roadways.

## Treatment of Roads With Brine

The need is there: the funds are not. Each year money to construct these road networks is being limited by inflation. The most economical solution in many cases will be soil stabilization using the chloride salts such as $MgCl_2$.

Historically, cheaper salts such as sodium chloride or calcium chloride were used preferentially to the more expensive magnesium chloride for soil stabilization and road building, even though the hygroscopic nature of magnesium chloride makes it a better salt for this application. Because the magnesium chloride solution is a by-product in the production of titanium metal, it is now offered at a

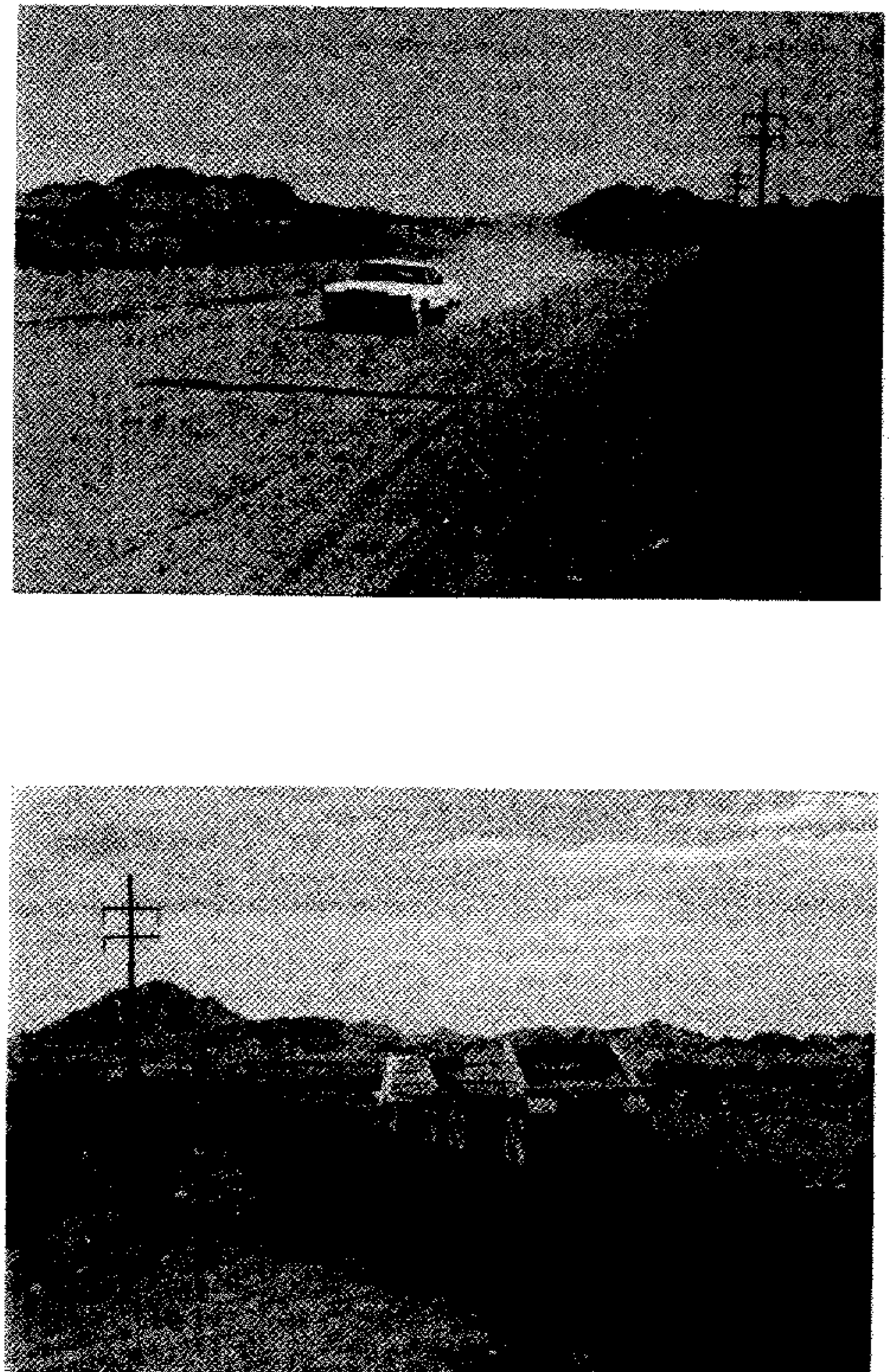

**Figure 4.** Pabco Road before and after treatment with TIMET's $MgCl_2$ solution.

TABLE 2

Dust control methods

| Suppression Method | Projected Life | Application Rate | Estimated Costs: Material | Labor | Monthly Averages |
|---|---|---|---|---|---|
| Paving | 20 years | Once | —$90,000— | | $ 375 |
| Oil Treatment | 1–5 years | 6,000 gal/acre | $8,000 | $1,000 | $ 750 |
| Water Treating | 3–5 hours | 3,000 gal/acre | $ 15 | $ 100 | $3,350* |
| Other Chemical Suppressants | 30 days–1 year | 3,000 gal/acre | $ 200 | $ 100 | $ 300 |
| TIMET Magnesium Chloride Solution | 60 days–1 year | 2,500 gal/acre | $ 120 | $ 100 | $ 120 |

*Based on watering once per day.
One mile of 16-foot-wide road bed is equal to two acres.

price competitive with the other salts. Five years of testing shows it to be a very effective soil stabilizer.

A typical application rate is 15 tons per acre or 15 tons per 8-foot-wide strip, one mile long. During the first year, four applications are recommended. After that, once or twice per year should be sufficient, depending on soil type and traffic conditions.

The following is a list of typical applications:

*Off-Road Racing.* A major one-day source of dust in Clark County, Nevada has been an off-road race. During the 1980, 1981 and 1982 races, five miles of the track and the parking lot were treated. The results were very good with a control factor of greater than 80% on the race track and 95% on the parking lot.

*Pabco Road Treatment.* Pabco Road in the southeast Las Vegas (Nevada) valley is a major fugitive dust source. Relatively heavy traffic and large trucks caused significant dust problems. This road has been treated as required for the past four years. The treatment has abated this dust greater than 90% (see Figure 4). A 10-hour traffic count on June 16, 1982 showed 240 cars and pickups plus 350 gravel trucks with a minimum of dust problems.

*Hotel Parking Lot.* A twenty-acre parking lot was treated, resulting in a greater than 90% reduction of dust.

*McCarren International Airport.* Construction areas and berms alongside runways, plus overflow parking areas.

*County Roads.* Approximately 1,600 miles of county graveled roads have been treated. This includes roadways in four states-Nevada, Utah, California and Arizona.

*Cost Effectiveness.* The estimated average monthly cost per mile for various methods of dust control was calculated (see Table 2).

## ACKNOWLEDGMENTS

The authors are indebted to M. J. Miles of the Henderson Technical Laboratory for his analytical and bench scale services and to Abraham Sadan for his consulting services.

## REFERENCES

Israel, R. W. 1982. Soil Stabilization and Cold Mix Recycling, Bomag, U.S.A., Springfield, Ohio.

Salt Institute. 1975. Salt for Road Stabilization. Alexandria, Virginia.