

Natural Sodium Sulfate in North America

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ABSTRACT

Large deposits of the decahydrate of sodium sulfate are found in the prairies of North America, located mainly in southern Saskatchewan, but also in North Dakota, Montana, and Alberta. These deposits are of sufficient quantity and quality to justify commercial development for their exploitation.

Sodium sulfate on this continent occurs as brine or in beds of intermittent and/or permanent crystals. Most beds are contaminated with various amounts of silt, sand and decayed organic matter. Soluble impurities such as chlorides, carbonates and by-carbonates of sodium and sulfates of magnesium and calcium are leached from the soil of the run-off area surrounding the deposits.

This paper deals with the origin of sodium sulfate, and the physical and chemical aspects related to the sodium sulfate industry. The problems of garnering raw material, refining and dehydration are discussed with emphasis on the plants of Saskatchewan Minerals at Chaplin, Bishopric, and Ingebrigt. The principal uses of sodium sulfate are also discussed.

INTRODUCTION

Sodium sulfate is deposited in numerous saline lakes and "alkali sloughs" in the southern part of Saskatchewan, North Dakota, Montana, Wyoming, and Washington. It occurs around and beneath the lakes as beds of intermittent crystals or brine. The crystalline form is called "mirabilite" ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) or Glauber's salt, named after Johann Wilhelm Glauber in 1658, a German chemist who had prepared the salt by treating sodium chloride

with sulphuric acid. The anhydrous form of sodium sulfate is "thenardite" (Na_2SO_4) and occurs rarely in nature.

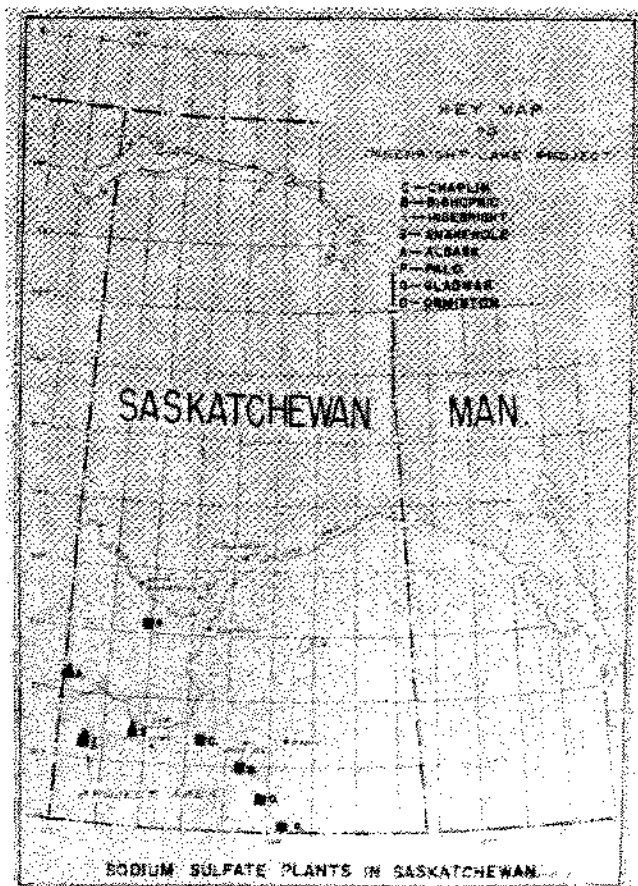


Figure 1. Map of Saskatchewan.

Extensive investigations of the sulfate lakes in the prairies during the twenties by L. Heber Cole (1926) and more recently by R.V. Tomkins (1954) have shown that a number of large deposits of sodium sulfate are sufficient in quantity and quality to justify commercial development.

The first production of natural sodium sulfate in Saskatchewan goes back to 1918. However, the success attending these efforts have varied and many failures occurred due to inefficient operating methods and the market instability at that time.

GEOLOGY AND ORIGIN OF SODIUM SULFATE DEPOSITS

Natural deposits of the decahydrate of sodium sulfate are the result of normal geological processes. They are worldwide in occurrence and are found in depressions, without outlets, of arid and semi-arid regions.

Sodium sulfate deposits differ in their origin from those of sodium chlorides or potash. Sodium sulfate is of post glacial origin, and may have been leached out of the soil surrounding the deposits while the chlorides and potash salts are the evaporites of fossil seawater cut off from an ancient ocean.

From the time meteoric water starts to dissolve material until the solution reaches the sea, it undergoes many vicissitudes of solution, precipitation, resolution, and changes. Surface water has a relatively large proportion of sulfates and carbonates, and a small amount of chlorides. On the contrary, seawater has very small amounts of sulfates, much less carbonates, and a large amount of chlorides because the carbonates and sulfates have been removed to form limestone, dolomite, magnesite and gypsum.

The composition of the evaporites we are dealing with varies according to the geology of their drainage basins. During the glacial epoch the western plains of Canada were covered by continental glaciers which advanced from a center situated somewhere west of the Hudson Bay. Such glaciers scattered boulders and dedrital material from the Laurentian Plateau over the western plains almost to the Alberta foothills where they met glacial ice flowing eastwards from the Rocky Mountains. The soft rock formations of the plains was the source of the fine grained till. The material from several formations have been intermixed to form the glacial deposits upon which is developed the soil.

There are three principal problems concerning the origins of the sodium sulfate deposits:

1. The origin of the lake basins
2. The source of the sodium sulfate
3. The agent and the manner of transportation and the deposition of the sodium sulfate.

It is obvious that these deposits can form only in comparatively dry climates where evaporation exceeds precipitation and today they can be found only in equally arid regions. Most sodium sulfate deposits in North America are exposed to weathering. They are locally protected from surface water seepage by impervious layers of clay, till, or stone. Mineral deposits of this class are referred to as evaporites. Most connate evaporites are overlain by substantial amounts of overburden. The sodium sulfate deposits, on the contrary, are surface deposits occurring as crystalline beds from a few inches to many feet in thickness, and in rare occasions reaching 100 to 140 feet. These beds are often covered with a few inches of irregular and impure crystalline masses and brine differing in depth and density according to location and temperature at any particular time of the year.

Origin of the lake basins.

All of the large deposits of sodium sulfate are to be found in the lowest lying areas without drainage outlets. A.E. Christiansen (Sask. Research Council Map 3) prepared a map showing the preglacial valleys which is based on core drillings. It was of great interest to notice that all major deposits of sodium and magnesium sulfates are located in these preglacial valleys (Figs. 2 & 3).

Advancing glaciers may have filled the preglacial valleys with huge blocks of ice which were later covered with sand and gravel or other types of moraine. The covered ice blocks eventually melted and left undrained basins and kettle holes in which the sodium sulfate is now deposited.

Erosion has modified these moraines to some extent and dissected the till which now covers the area. The vast amount of moraine material deposited over the western plains undoubtedly altered some preglacial valleys, created huge terminal moraines and formed valleys with chains of numerous undrained basins and lakes (Fig. 4).

These preglacial valleys are not only of importance for their salt deposits but also contain excellent aquifers 200 to 400 feet beneath the deposit (Fig. 5).

Theories on the source of sodium sulfate.

A number of theories have been presented to explain the origin of the sodium sulfate deposits. The most commonly accepted one is the ion

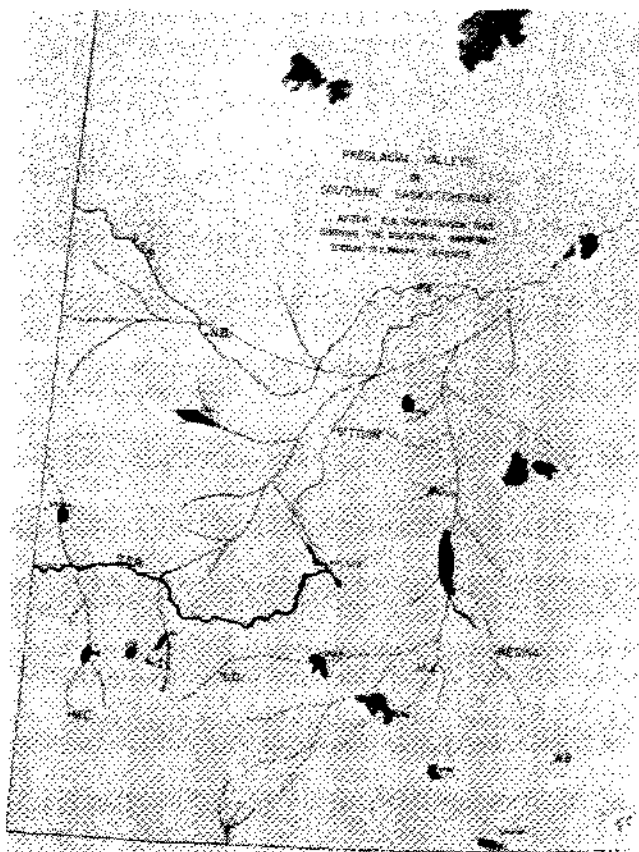


Figure 2. Map of the known preglacial valleys in Saskatchewan. Note: almost all large sodium sulfate deposits are located in preglacial valley, except Ormiston and Gladmar. This area is not test drilled yet.

exchange theory. There is no doubt that most sodium sulfate results from the weathering of glacial drift or bedrock. For example, the calcium ion of gypsum (CaSO_4) may be exchanged with the sodium ion of bentonite.

Renick (1924) describes the hypothetical reactions as follows:

Na base exchange silicate + CaSO_4 or MgSO_4

Ca base exchange silicate + Na_2SO_4 or K_2SO_4

Cole (1926) in his extensive report describes an experiment which proves Renick's theory. Although some other theories are conflicting, the ion exchange theory forwarded by Renick (1924) and experimentally demonstrated by Cole (1926) can be reasonably accepted as the origin of sodium sulfate in the prairies.

Transportation and deposition of sodium sulfate.

Solutions of sodium sulfate are probably carried into these undrained basins by the spring run-off waters from the drainage basins in which the deposits are located. Ingebrigtsen Lake for example, is covered, after break-up time in the spring, with 12 to 24 inches of water which usually has evaporated by June or July. Data obtained from the Meteorological Division of the Department of Transport for the Ingebrigtsen area show that the long term yearly average precipitation of nine inches is exceeded by an evaporation of 36 inches. Therefore, the salt carried in by the meteoric waters must be deposited as salt beds.

Most salt lakes are fed by a number of springs in their vicinity. A few of the springs draining into the lake contain varying amounts of sodium sulfate up to 1,000 ppm. According to Tomkins (1954), if the inflow to a basin were 100 gallons per minute the deposition of the 3 million tons of sodium

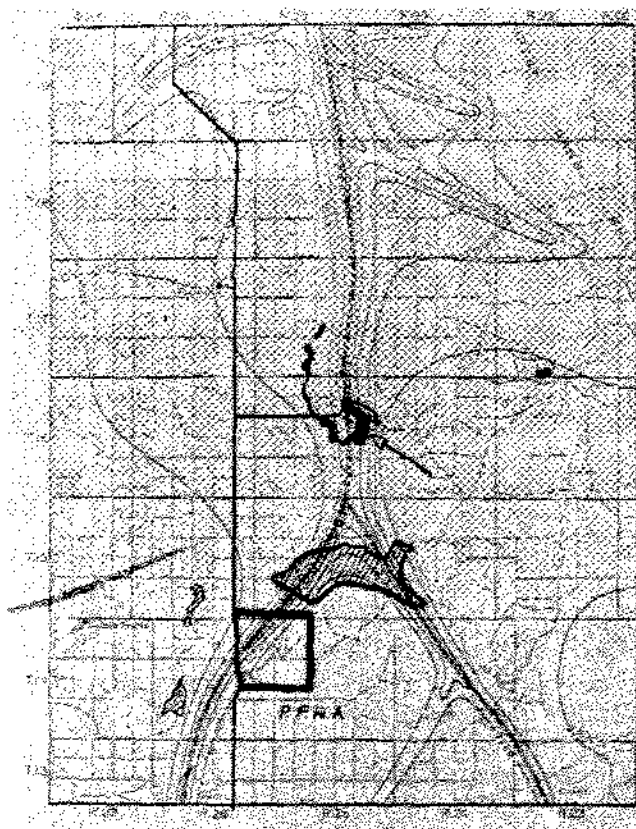


Figure 3. Bedrock surface topography of the Ingebrigtsen area.

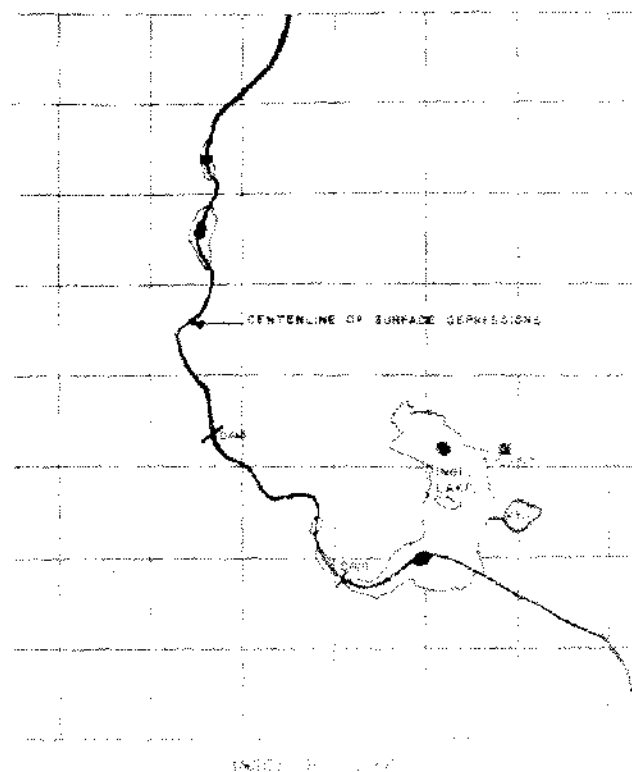


Figure 4. Map showing regional topographic setting.

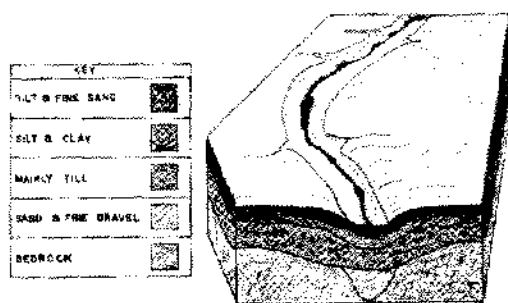


Figure 5. Schematic geological cross section of buried preglacial valley.

sulfate would require 12 thousand years. This is a reasonable length of time for the formation of a post glacial deposit.

If we accept the spring theory we must account for the origin of sodium sulfate in spring water. Springs could obtain their dissolved solids from previously deposited salts or buried saltbeds. Systematic oil drillings have revealed only one buried salt bed in the Ingebrigt area.

It is very doubtful that the springs near the lakes acquire their salt by flowing through existing salt beds. Cole (1926) reports that a pipe driven into the orifice of a spring in Muskiki Lake contains only one-third of the dissolved solids of a sample taken at the mouth of the same spring. At Ingebrigt Lake a strong flowing spring kept an orifice in the ice open and built up a mound of ice and salt around it. In spring the ice melted away and the salt remained until water dissolved the mound (Fig. 7). The mound of salt is definite proof that the spring water contained dissolved salt. However, because recent pumping has lowered the water table in the underlying aquifer, the spring has ceased to reproduce this phenomena during the last three winters.

The most reasonable theory for the creation of the depressions which contain the sodium sulfate deposits is as follows: (1) advancing ice sheets fill in preglacial valleys and cover their alluvial gravel beds with more sand and gravel derived from melt-water, (2) later more ice may have covered the valley fill material, (3) at a pause in the advance of the glacier the ice in the preglacial valley was covered with till and other glacial debris, (4) retreat and melting of buried ice developed the kettle holes and depressions. The occurrence of more than one period of glaciation complicates the picture with the development of new channels, side channels and the burial of existing valleys and channels (Fig. 6).

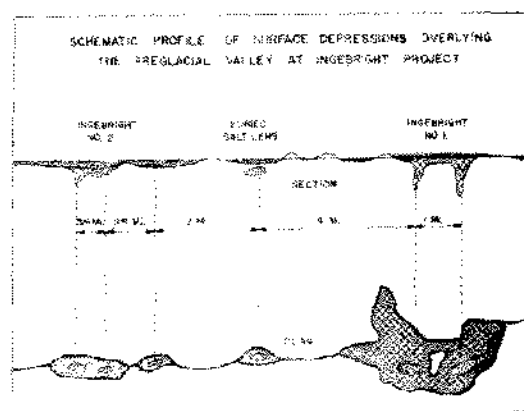


Figure 6. Schematic profile of surface depressions overlying the preglacial valley at Ingebrigt project.

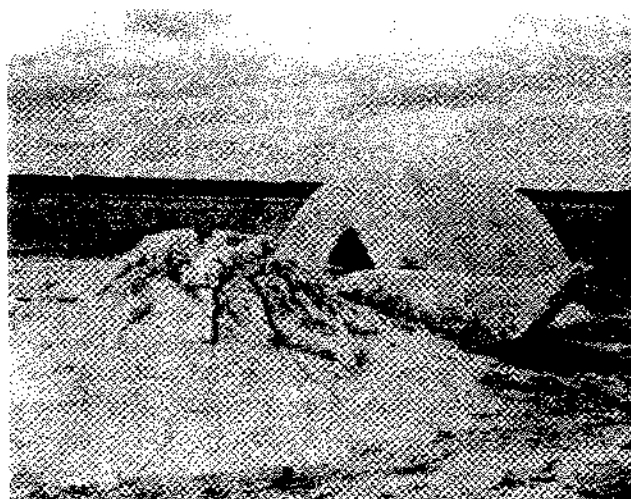


Figure 7. Mound of sodium sulfate in the Ingehrigt Lake caused by a flowing spring during the winter. In April-May the ice thawed out and the salt was left behind.

PHYSICAL AND CHEMICAL PROPERTIES OF SODIUM SULPHATE

Before entering into the discussion on the technology of sodium sulfate production it may be well to review some of the chemical and physical characteristics of sodium sulfate.

(a) Mirabilite, or Glauber's salt, is defined as Na_2SO_4 combined with ten molecules of water. The ten molecules of crystal-bound water account for 55.9% of the weight of the crystals ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). Therefore it is very advantageous to remove the water prior to shipment. The crystals are monoclinic, white, transparent to opaque and occur readily in nature (Fig. 10).

(b) Thenardite, or anhydrous sodium sulfate, is defined as Na_2SO_4 and is found sparsely in nature. It forms orthorhombic crystals and twinned crystals (Fig. 11).

According to Mellor (1922) anhydrous sodium sulfate can occur in four forms depending upon the method of and the temperature at which the formation of the salt occurs. Briefly:

1. Thenardite is stable below 91.4°F . It is very hygroscopic below 77°F and forms decahydrate.
2. The second form occurs when heated to 356°F . It will not take up water of hydration.
3. The third form is produced when molten Na_2SO_4 cools and is exposed to air causing it to return to the second form.

4. The fourth form of Na_2SO_4 exists only above 932°F .

Most manufacturers of natural sodium sulfate have difficulties in making a free flowing product caused mainly by the above mentioned forms of Na_2SO_4 (Burr, 1951).

The decahydrate of Glauber's salt and the anhydrous form are the most important. However, there is an intermediate form, a hepta hydrate, containing seven molecules of H_2O . It is an unstable phase and is of secondary importance in sodium sulfate technology. Sodium sulfate can occur in several combinations. It normally occurs:

- (1) with sodium carbonate (Na_2CO_3) as Burkeite.
- (2) with calcium sulfate (CaSO_4) as Glauberite.
- (3) with magnesium sulfate (MgSO_4) as Vantsoffite.

A list of all minerals which contain Na_2SO_4 is beyond the scope of this paper.

Solubility of sodium sulfate.

The solubility and the crystallization properties of sodium sulfate play a major role in sodium sulfate production. These properties are well known. Unlike many compounds, the solubility of sodium sulfate in water does not increase linearly with temperature rise. Variations in data exist due to different procedures in determining the data and difficulties in obtaining experimental accuracy. The temperature at which Glauber's salt melts in its own water of crystallization is accepted by most authorities as 90.2°F . This is true when heating is conducted in an open vessel and assuming one atmosphere of pressure. However, the theoretical quadruple point, at which decahydrate, anhydrous salt, a saturated solution and vapor are present in equilibrium under the vapor pressure of the system is 90.7°F according to Taylor (1931) (Fig. 12).

Between 32°F and 29.8°F there can be an equilibrium between ice, solution and vapor. If cooling is continued the formation of two solid phases, ice and Glauber's salt will result.

As the temperature rises above 32°F there is an equilibrium between Glauber's salt, solution and vapor with increasing amounts of Na_2SO_4 being soluble in a given amount of water.

Above 90.2°F there is a break in the curve. Above this temperature the anhydrous salt Na_2SO_4 begins to precipitate out and decreasing amounts will remain in solution at higher temperatures.

On raising a solution containing 100 grams of water and 78.6 grams of Na_2SO_4 to 60°C (140°F) the anhydrous Na_2SO_4 would precipitate leaving only 46 grams in solution. If no water were lost by using a condenser the original composition would remain the same.

At 127°C (257°F) the minimum solubility occurs and at 233°C (453°F) the solubility increases again slightly. Only 45 grams of Na_2SO_4 are left of the original amount of 178.6 grams of Glauber's salt. By reaching point "G" an equilibrium exists of four phases; monoclinic and rhombic, anhydrous Na_2SO_4 , a solution and vapor. The overall composition is not altered provided no water is evaporated. Only the phases have changed.

Providing pressure equipment is used and providing the temperature is increased to the critical temperature of 366°C (689°F) all 78.6 grams of Na_2SO_4 originally present in the Glauber's salt is precipitated as anhydrous Na_2SO_4 and the 100 grams of water approaches H_2O in composition. If these conditions can be met technically then this procedure could be employed industrially. However, the cost and mechanical difficulties would probably exclude this method from the production of commercially profitable saltcake (Fig. 13).

Other combinations.

So far we have dealt with only one solution containing Na_2SO_4 and water. All values given in the previous chapter from the International Critical Tables change when a solution contains double, triple or multiple salts. In most of the natural deposits in Canada there are MgSO_4 , CaSO_4 , NaCl , Na_2CO_3 , $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$ and lesser amounts of other minerals present.

NATURAL SODIUM SULFATE DEPOSITS

Natural brine deposits in the United States were developed prior to World War I. Production from natural brine rapidly expanded after the outbreak of the war cut off European supplies. In Canada the deposits of Saskatchewan consist of Glauber's salt either as intermittent crystals or permanent crystals. Brine covers these alkali lakes only after the break up in spring until freeze up.

At present sodium sulfate in the United States is produced from complex brines drawn from sources 90 to 150 feet below the surface of Searles Lake which is located approximately 180 miles northeast of Los Angeles (Figs. 31, 32 & 33). Another complex brine containing Na_2SO_4 occurs in Great Salt Lake, where a plant with a capacity of

200,000 tons per year of Na_2SO_4 will be in operation by 1971.

From less complex brines sodium sulfate is produced in Monhans, Brownsville and Cedar Lake in Texas. Other sources or deposits are found at Verde Valley, Arizona; Soda Lake at Carrizo Plain, San Luis Obispo County, California. At Wabuska Lyon County, Nevada. In New Mexico a deposit is located ten miles west of Alamogordo.

A number of less extensive deposits are located in North Dakota, Montana, Wyoming and Washington. In many respects the latter deposits are very similar to the deposits in Western Canada.

At the Great Salt Lake near Ogden, Utah, the Lithium Corporation of America and Chemsalt (a subsidiary of Salzdethfurth, A.G.) are building 12,000 acres of solar ponds.

The production processes where brine is pumped from subsurface fields in California, Texas and Mexico are essentially the same as those where brine is made on the surface of the Glauber's salt beds of the Canadian lakes. The high density brine is chilled to precipitate the Glauber's and then this raw material is dehydrated. In the warmer climate of the south the chilling has to be done in elaborate refrigerating systems while the cooling of the brine and fractional crystallization in Canada occurs naturally in brine lagoons or reservoirs.

INDUSTRIAL WATER SUPPLY AT INGBRIGT LAKE

Sufficient fresh water is a prerequisite to the operation of any sodium sulfate plant, regardless of the means of garnering of raw material. The location of a supply of economical fresh water was extremely difficult due to the complex geology of the Ingebrigt area and its geographical location.

The proposal to construct a 600 ton per day sodium sulfate plant at Ingebrigt Lake rested solely on the availability of water.

Considerations were given to the construction of a 50 mile water pipeline from the South Saskatchewan River to the lake site, however, preliminary cost estimates of such a pipeline called for a capital outlay of approximately 3 to 4 million dollars not including pumping stations and a water storage reservoir. A shorter pipeline from nearby Big Stick Lake would have been less costly, but this lake has a history of being periodically dry. According to the Prairie Farm Rehabilitation Administration (P.F.R.A.) one can anticipate 2,000 acre-feet only one year in every four; 8,000 acre-feet one year in every five; and 20,000 acre-feet one year in every ten years from Big Stick Lake.

To operate a 600 ton per day sodium sulfate plant requires a minimum of approximately 2,000 acre-feet of water if the brining system is used. Plans for any of these pipelines were abandoned in favor of an extensive ground water investigation.

Adjacent to the Big Stick Lake the P.F.R.A. maintains an extensive irrigation project at an area called "the Lower V." This area is located in a widened valley seemingly a preglacial valley (Fig. 3). Ingebrig Lake lies in the same valley, approximately 14 miles north of the P.F.R.A. project.

The water for the P.F.R.A. irrigation project is supplied by pumps delivering a maximum of 900 gallons per minute. This fact encouraged us to carry out a large scale drilling program at Ingebrig in an attempt to locate an adequate water supply.

The investigation was carried out by a consulting firm. On a trial and error basis 65 testholes were drilled. This intensive test drilling revealed that the surface depression in which the two Ingebrig Lakes and a number of alkali sloughs are located is a "V" shaped valley with steep sides approximately 200 to 300 feet deep and 800 feet wide at the top (Fig. 5). The "V" shaped valley is either of preglacial origin or was cut into the bedrock by the melting water of a retreating glacier and was filled with more than 200 feet of water bearing stratified silts, sands and gravel. The alluviation must have covered large blocks of ice resulting in huge kettles filled with sodium sulfate. The largest kettle is 139 feet deep and approximately one mile wide at the 20 foot contour line (Fig. 8).

Three high capacity production wells, each delivering 500 gpm, were developed and are operated on a year round basis. Periodic observation of water levels in the aquifer have been taken continuously for nearly two years.

A fresh water reservoir was constructed by damming off a section of the valley in which the Ingebrig chain lies. The fresh water pumps are located outside the dams holding the fresh water (Fig. 9).

"Brine make-up water" can be drained onto the deposit from this water storage whenever required. To overcome the disadvantage of a small lake surface, it is necessary to keep a shallow layer of water on the salt bed. The water temperature rises much faster when a 6 inch layer of water is employed than when a 36 inch body of water covers the salt deposit (Fig. 14). Furthermore, the mixing action by wind penetrates faster to the interface of salt and brine in a shallow lake than in a deep lake. The mixing of weak but warm surface brine with the saturated cool brine at the interface rapidly increases the brine density. When the lake brine has

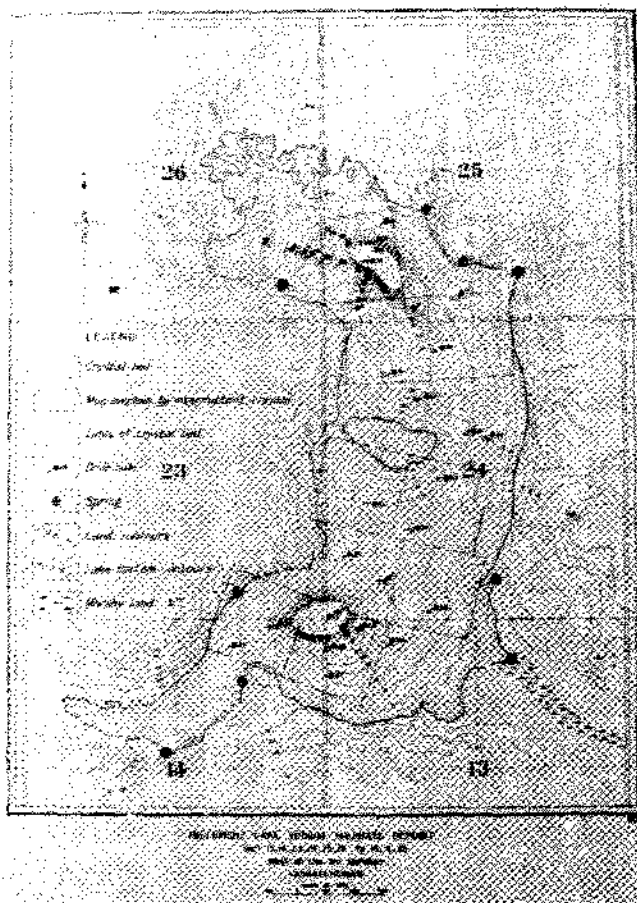


Figure 8. Springs and isopach of sodium sulfate deposit (after L.H. Cole).

reached its desired density it is pumped by large pumps (capacity approximately 20,000 gpm) into the lagoons or brine reservoirs (Fig. 15). All or most of the mud intermixed with the permanent bed is left behind. During the autumn months the brine cools and the maximum amount of Glauber's salt is allowed to crystallize out while most of the other salts considered as soluble impurities remain in solution. The dilute brine is drained back through controlled gates (Fig. 16) to the lake or into other holding ponds before ice forms on the surface or before unwanted salts start to precipitate in the ponds. By the time the dilute brine has been completely drawn off, frost has arrived and bulldozers or draglines can windrow the four to five feet thick layer of Glauber's salt. The windrowing facilities further drainage and allows frost to penetrate to the bottom of the brine reservoir. Conventional earthmoving equipment transfer the raw salt to a stockpile (Fig. 17). This portion of the harvesting begins in early December and is usually completed by the middle of February depending

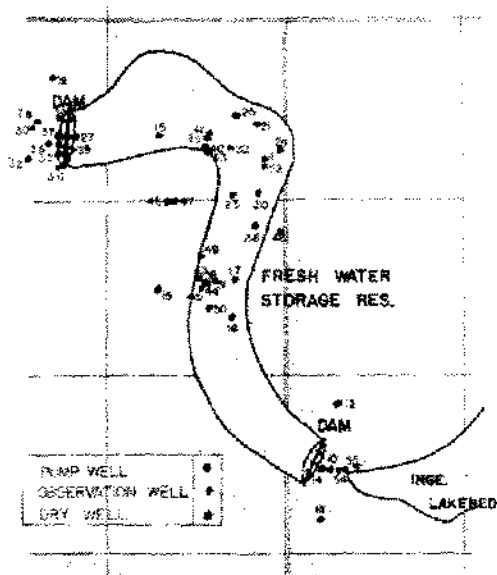


Figure 9. Fresh water storage holding 500,000,000 gallons.

on the weather and on the amount of equipment employed.

Summarizing the advantages of the brining system; it is obvious that the brining process is superior to all other harvesting methods known both economically and from a purity point of view. All natural sodium sulfate deposits contain more or less insoluble and soluble impurities. The insolubles originate from sand and silt carried in by the spring run-off waters or by high winds. Algae and brine shrimp contribute to the decaying organic material. The soluble impurities originate in the same way as the sodium sulfate; being leached out of the soil of the surrounding drainage area. The insolubles are either enclosed in the Glauber crystals or occur in stratified layers throughout the crystal bed. The brine, however, is relatively free from dirt contamination which settles out. The chemical impurities are reduced to a minimum by fractional crystallization because sodium sulfate crystallizes out first while the other salts remain in solution and are drained off. Economically, it is superior to direct mining since only control ditches, gates, fresh water storage and brine lagoons have to be constructed.

HARVESTING RAW MATERIAL

The methods whereby the material is harvested and brought to the plant vary considerably. In Cali-

fornia, Texas, and Mexico, where the deposits are located at a considerable depth, the brine is brought up to the surface through a system of wells then gathered in collecting tanks and piped to the plant. This operation may be carried out throughout the whole year around. In Canada the harvest is limited to the frost-free season only and the capacity of the plant is very often not determined by the size of the production machinery but rather by the amount of raw salt that can be harvested in the frost-free season of one year.



Figure 10. Mirabilite, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ decahydrate.



Figure 11. Thenardite, Na_2SO_4 anhydrous.

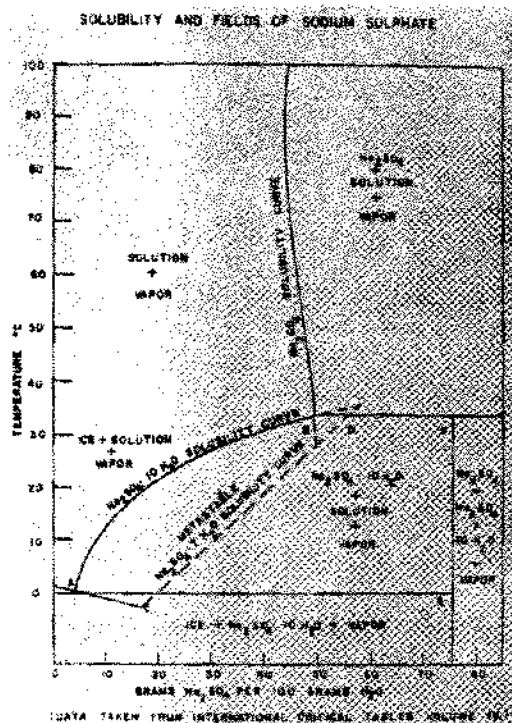


Figure 12. Phase diagram.

Direct mining.

In the early days of sodium sulfate manufacturing salt was acquired by direct mining. Where a hard five to six feet thick bed of fairly clean crystals occurs direct mining by blasting followed by mechanical loading and hauling into a washing plant or stockpile is carried out. This type of winning raw material may be carried out on a year round basis. The method requires only water for washing the insolubles out of the crystals.

Dredging.

One Canadian producer is employing a dredge to provide raw material besides using the brining system. The dredging can be started in early spring and continued until the fall freeze-up and has the advantage that only a dredge operator is needed to bring the raw material to the plant. The disadvantage is the high initial investment for the dredge and the washing plant. However, if the brining system is limited by the small surface area of a deposit and/or lack of water, dredging is perhaps the best possible way of supplying raw material.

Some sodium sulfate producers rely on gathering the almost pure intermittent crystals which are scraped off the lake's surface as soon as the frost permits the bringing of machinery onto the salt

bed of the lake or when the permanent salt bed of the lake or when the permanent salt bed is hard enough to carry heavy machinery and enough intermittent crystals have precipitated. A special loader may be required to scrape off a thin layer of one to two inches of intermittent crystals efficiently.

One problem faces the user of an intermittent bed and also the user of the brining system and that is the fluctuation of the water level of the lake. In seasons of extremely high rainfall the water level may remain high and the water cannot warm up fast enough to permit the salt of the permanent bed to dissolve the required amount of salt. Whereas in a season of drought, there may be insufficient brine on the lake to guarantee a large enough supply of intermittent crystals or brine if the brining system is used.

Brining system or surface solution mining.

Saltcake producers using the brining system rely almost as much on the weather as does a farmer. Sufficient water and solar energy are required to provide a strong brine and enough of it. The brin-

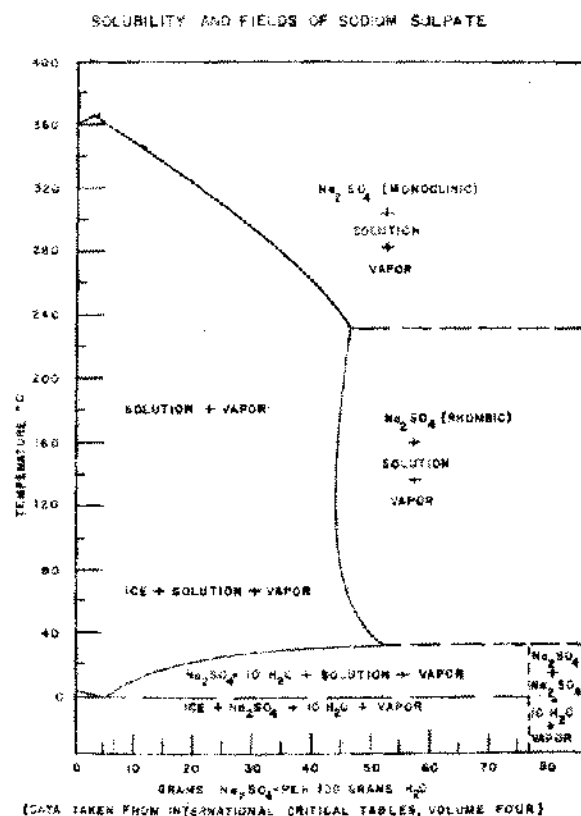


Figure 13. Phase diagram.

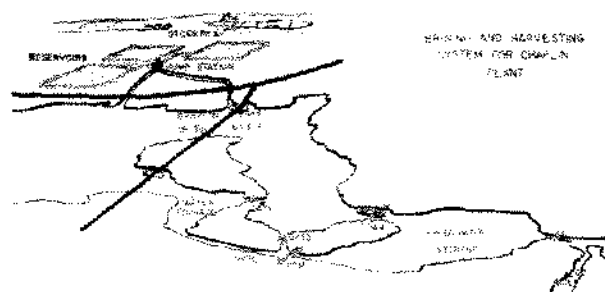


Figure 14. Chaplin brining and harvesting system. Fresh water storage, lake brine reservoir, stockpile and factory schematically.

ing system is superior to all other methods of gathering raw material providing the lake surface is large enough and the water level of the lake can readily be controlled. In our plants at Chaplin and Bishopric we have sufficient large fresh water storage to supply "make-up water" for brine and to take care of the loss by evaporation. They are filled in spring either by gravity flow or by pumps from nearby rivers or lakes (Fig. 14). At our Ingebrigt project the fresh water storage is replenished by subsurface water. Three deep wells supply 500 gallons per minute each as required.

Ingebrigt lake covers only 840 acres with approximately 700 acres of crystal bed compared to Chaplin lake with a surface area of approximately 11,520 acres. To produce 100,000 tons of saltcake per year a minimum of 350 to 400 thousand tons of raw material (Glauber's salt) has to be brought into solution. The solubility of sodium sulfate is almost a straight function of temperature and the saltcake producer prefers a thin layer of four to six inches to achieve the maximum utilization of the sun energy. In 1968 brine temperature of 94°F were recorded. Therefore it is preferable to keep the brine level shallow. When the desired brine density is reached the brine is transferred by pumps into the brine reservoir (crystallization pond) and the lake surface is flooded again with fresh water to make up a new batch of brine. It is of great advantage when the saturated brine at the interface is disturbed or mixed either by wind or mechanical means.

At Ingebrigt we successfully use a tracked swamp vehicle to achieve the mixing which increases our brine harvest approximately 20 to 30 per cent.

In order to increase the absorption rate of energy we dyed the brine dark in testing ponds.

However, this had to be abandoned because the dye interfered with the color of the saltcake.

BRINE COOLING AND FRACTIONAL CRYSTALLIZATION

In the previous chapter methods of improving energy and mass transfer to increase the rate of salt solution were described. Now we are concerned with the release of this energy to increase the precipitation rate.

The high density brine averaging 20 to 25 per cent of Na_2SO_4 in solution (maximum saturation point 33 per cent at 92°F) is stored in the brine reservoir to be chilled. Besides sodium sulfate the brine contains dissolved soluble impurities such as NaCl , MgSO_4 , CaSO_4 , CaCO_3 , and CaHCO_3 .

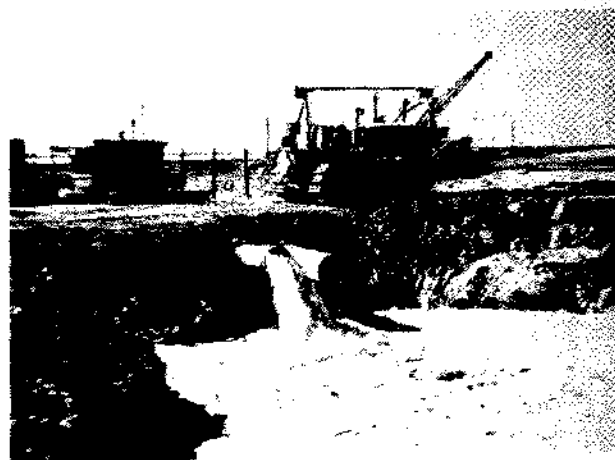
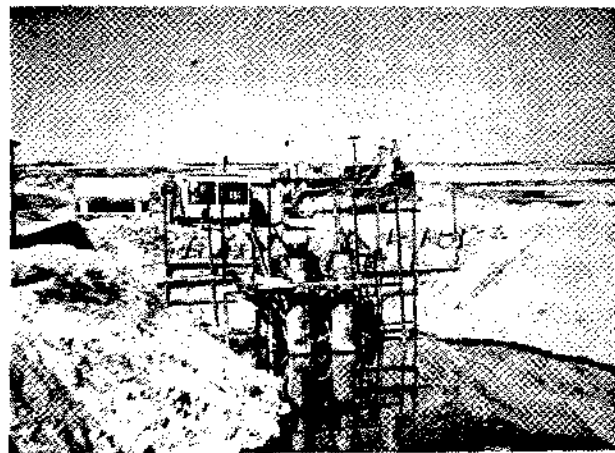


Figure 15. Brine pump, 20,000 gpm to pump brine from lake into brine reservoirs.

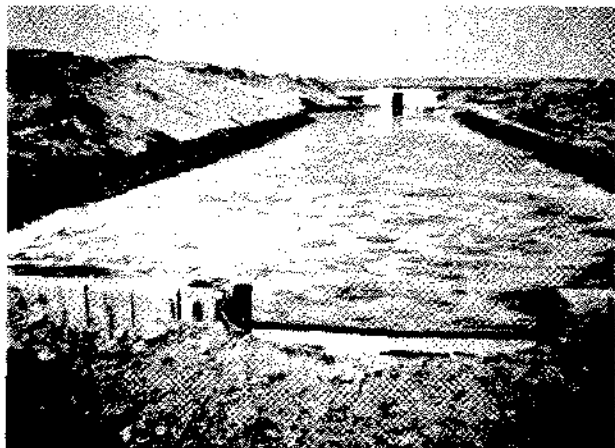


Figure 16. Pumping channel used as settling area. Note controllable gates at each side of channel.



Figure 17. Glauber's salt to be stockpiled.

Further, the brine includes various amounts of insoluble material such as suspended fine silt particles, decayed organic material originating from algae and brine shrimp. Most of these insolubles will settle out before the salt starts to precipitate.

Naturally, only the surface chills fast while the brine near the bottom is little effected by the surface cooling. The solar energy used to warm the water up and to dissolve the Na_2SO_4 is released when the salt precipitates out of solution and slows down the rate of surface cooling. The temperature gradient between the brine surface and the brine at the bottom of the reservoir is extremely steep. 30°F and ice formation has been observed on the

surface and 60 to 65°F has been registered three to four feet below.

The dilute brine should be drained before the ice forms. Ice cannot be removed from a reservoir and has to be evaporated. Originally, the cool and diluted top layer of brine had to be drained off and the warm brine underneath exposed to the chill and drained off in succession until the reservoirs were empty of brine. However, it is impossible to drain only the upper dilute stratum off of an area of 70 acres. When a cold spell threatens to form a layer of ice on the top of the reservoir, the drainage has to be speeded up which results in the loss of strong brine and consequently large quantities of salt. For example, if the average maximum dissolved salt in the reservoir is 22 per cent and the dilute brine contains 12 to 13 per cent, the total or 100 per cent harvest is represented in 9 to 10 per cent salts retained in the reservoir as crystals. Consequently it was our aim to mix the cold upper stratum with the warm brine on the bottom. By doing so we achieved three advantages:

1. We crystallized another two to three per cent of salt which represents an increase of 20 to 30 per cent of our total harvest.
2. The warmer brine of the bottom coming to the surface prevents the formation of ice.
3. The diluted brine having the same density on top and bottom and can be drained at once when desired.

Now the drainage is no longer dictated by the formation of ice on the top, rather than by this point on the phase diagram where undesirable salt such as MgSO_4 , NaCl , etc. would start to precipitate. In 1968, careful handling of this fractional crystallization resulted in a purity of up to 99.7 per cent at our Ingebrig plant and 99.3 per cent at our Chaplin plant.

Needless to say how welcome the increase of the harvest is in the light that the amount of harvested raw material may be the limiting factor for a plant capacity.

MANUFACTURING—DEHYDRATION

Power supply.

Most sodium sulfate manufacturers purchase their power from hydro stations. In our Ingebrig plant built in 1967 we implemented the "Total Power Concept."

Our generating system consists of three 552 H.P. Waukesha engines fueled by natural gas which provide shaft power to turn electrical generators

producing a maximum of 1,050 K.V.A. In addition seven 150 H.P. Waukesha engines drive compressors to supply the combustion air for the submerged combustion evaporators (Figs. 18 & 19).

Heat rejected from the exhaust system of the 10 Waukesha engines is utilized in the rotary kilns. The heat rejected from the engine cooling water is pumped through a water jacket enveloping the melters to facilitate the melting of the Glauber's salt. Part of the cooling water passes through a heat exchanger providing hot water for washing purposes.

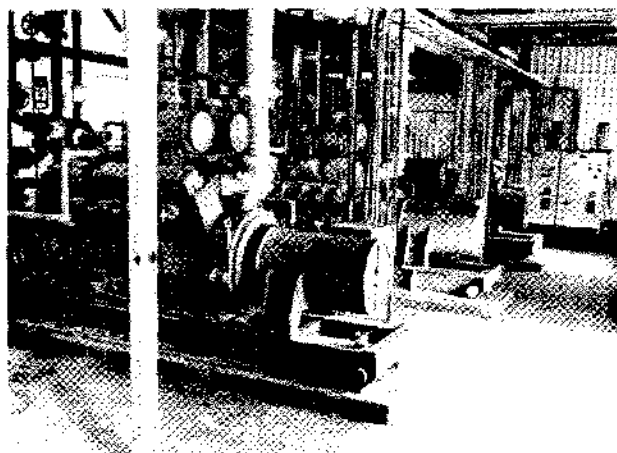


Figure 18. Three natural gas powered Waukesha engines (552 H.P. each) and 350 K.V.A. G.E. generators.

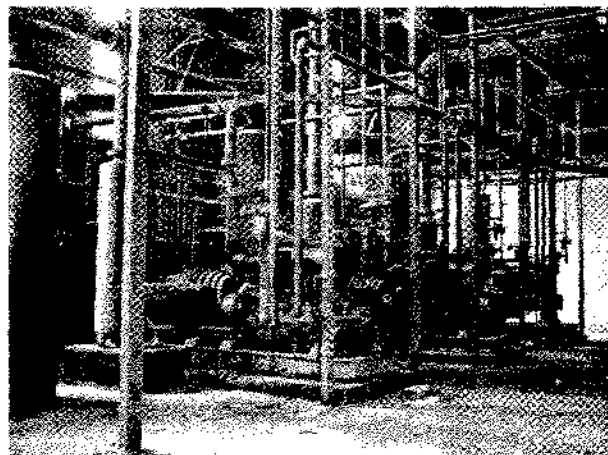


Figure 19. Three of seven natural gas powered Waukesha engines (150 H.P. each) driving air compressors.

This system makes the plant totally self-contained and assures the continuity of energy supplied when required. Economically, the "Total Power Concept" is very efficient. A feasibility study of Total Power versus Purchased Power in this particular instance proved that the Total Power is \$7,007 per year lower in operating costs at a 10 year depreciation on a 60,000 ton production level per year. After depreciation the saving amounts to \$18,800 per year or a total saving over a 20 year period of \$255,000.

Projected on a 150,000 ton production the saving would be as follows: At a 10 year depreciation, a saving of \$10,680 per year. After depreciation the annual saving would be \$22,480 or over a 20 year period the saving would amount to \$329,280 (Fig. 20).

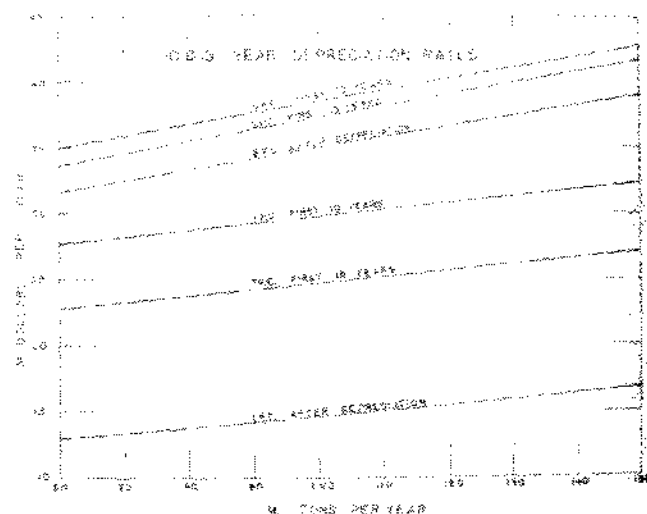


Figure 20. Cost of purchased power per year at a given rate of production versus cost of power produced at site using the Total Power Concept.

Refining and dehydration.

In most plants where raw material from natural deposits is used, the refining is limited to settling out insolubles during the brining season and the fractional crystallization which takes place in the brine reservoirs. This system is so efficient that a saltcake with a purity of 98.5 per cent to 99.5 per cent can be produced. (Saltcake is anhydrous sodium sulfate with a purity lower than 98 per cent).

In most sodium sulfate plants evaporation of the crystal bound water and sizing only is carried out.

In some plants additional refining and upgrading to a detergent grade (99.8 or 99.9 per cent) is carried out.

The methods of dehydrating Glauber's salt in use will be listed:

Convective or direct heat drying.

1. Rotary Dryers (Parallel and Counter Current Flow) (Figs. 21 & 22)

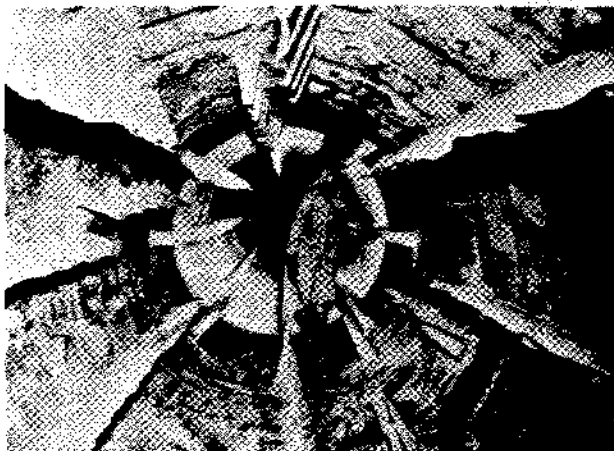


Figure 21. Inside of a counter current flow rotary dryer in Chaplin. Note the shiny stainless steel section in the west end of the kiln.

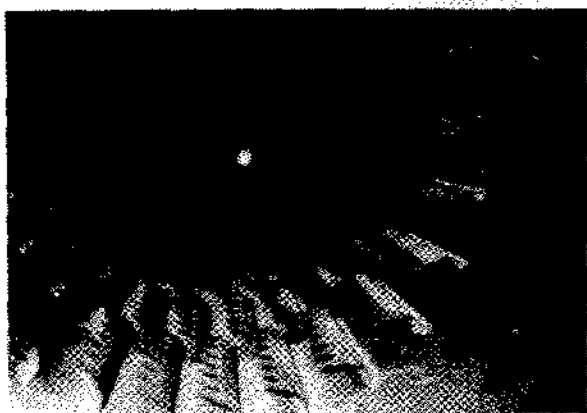


Figure 22. Parallel flow dryer at Ingebrigt. Note multitude of lifters compared to Figure 21.

2. Fluidized Bed Dryers
3. Holland Evaporator (modified spray dryer) (Fig. 23)

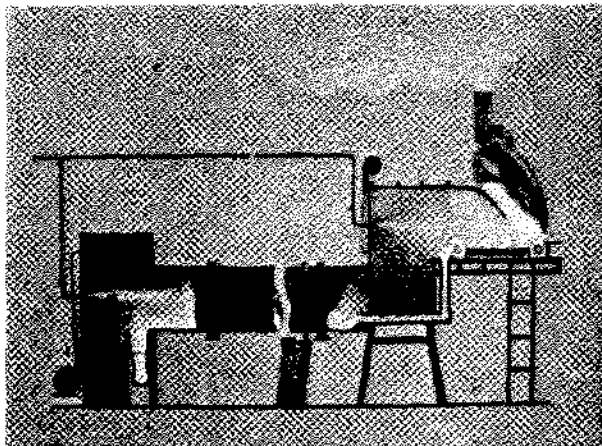


Figure 23. Holland evaporator and counter current flow dryer used in Chaplin and Bishopric (schematically).

4. Submerged Combustion Evaporators (Fig. 24)

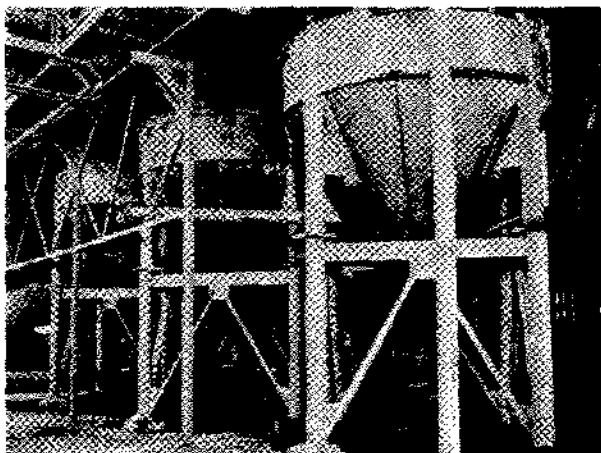


Figure 24. Submerged combustion evaporators capacity 18,000,000 BTU per hour.

5. Flash Dryers
6. Spray Dryers) Not longer in use to the knowledge of the author
7. Tray Dryers)

Conductive or indirect heat drying.

8. Multiple Effect Evaporators (Fig. 25)
9. Drum Dryers (Not in use)

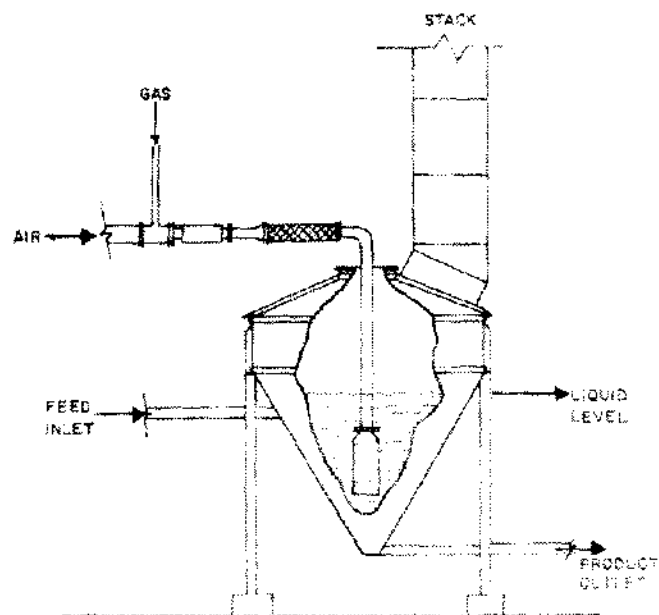


Figure 25. Schematic diagram of submerged combustion evaporator.

Precipitation processes.

10. Transition Deposition Point Precipitation
11. Precipitation of Sodium Sulfate with a Solid Precipitant (NaCl)
12. Precipitation of Sodium Sulfate using a Volatile Precipitant

The production methods have undergone considerable change since the first commercial production of sodium sulfate in the early twenties. However, the old conventional rotary kiln is still in use, improved and equipped with sophisticated instrumentation (Fig. 29). It seems that fluidized bed drying, not in commercial use as yet in the production of sodium sulfate, will seriously compete with the old dependable workhorse, the rotary kiln.

Fuel.

The types of fuel have changed too. Lignite coal was the first resource utilized to heat rotary kilns and is still in use in one plant south of Regina. Crude and bunker oil were in use until natural gas became available. With the availability of natural gas submerged combustion equipment could be employed. Today most manufacturers use a combination of either Holland, Submerged Combustion (Fig. 28) or Multiple Effect evaporators (Fig. 26) and rotary kilns for the final drying.

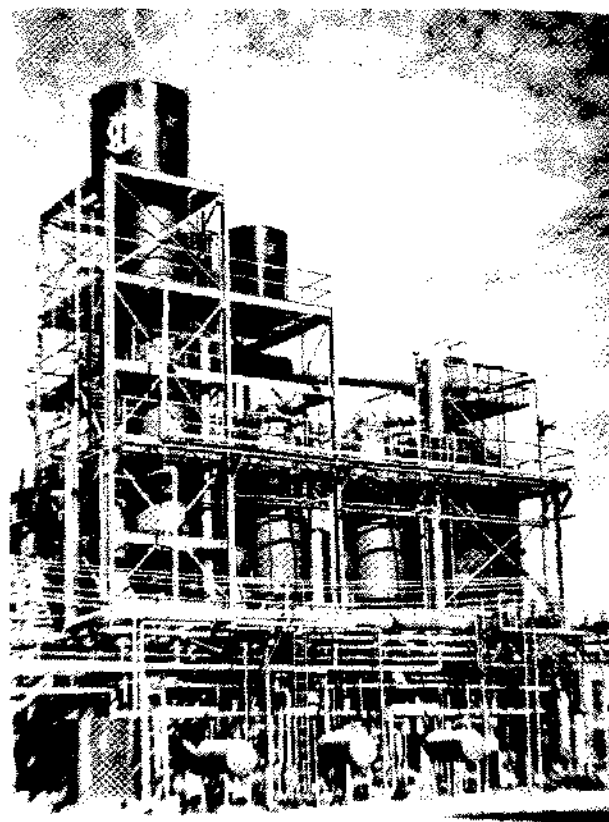


Figure 26. Multiple effect evaporator at Laguna del Ray, Mexico.

Materials handling.

Glauber's salt is moved by several types of conveying equipment. From the reservoirs to the stockpile most producers in Saskatchewan use conventional earthmoving equipment. Whereas from the stockpile into the plant conveyor belts, drag chains, and cable drags are employed. Inside the factory screw conveyors mostly move the salt and the thickened slurries. The finished product is crushed and different types of screening devices assure a uniform size of the product (Figs. 17 & 27).

Storage and shipping.

Anhydrous saltcake is very hygroscopic and must be protected against access of moisture. Storage facilities for the dry finished product vary in size and type considerably. In Chaplin we have a live storage capacity of 13,000 tons while the Ingebrigt storage facilitates 11,000 tons. A large



Figure 27. Raw salt feed conveyor and crusher. Note D8 crawler tractor pushing salt into the ramp at a rate of approximately 1,400 tons per day.

storage capacity is very advantageous, it assures a continuous production, independent from sporadic shipping spells, and allows a large inventory on hand to handle fluctuating requirements. Special shipments can be made immediately and operating or maintenance shutdowns can be bridged. Production can be planned avoiding fluctuation in the work force (Fig. 30).

USES OF SODIUM SULFATE

Most of the saltcake produced by us is used in the kraft pulp industry to free the cellulose fibres from the lignin, hemi cellulose and minor amounts of extractives. In the sulfate and sulfite processes the lignin is removed during the pulping while in the neutral sulfite semi-chemical pulping process only half of the lignin is removed during pulping. Ground wood or wood chips are cooked in the presence of sodium sulfate or sulfite in a digester. The lignin combines in the sulfite liquor to liginosulfonic acid and with sodium sulfate to a

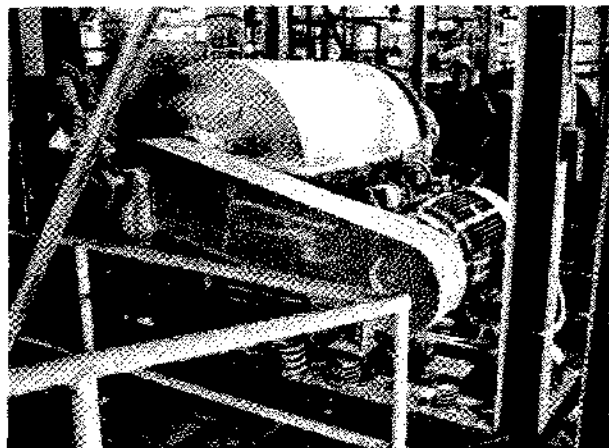


Figure 28. Submerged combustion evaporators, burner capacity 15,000 BTU's per hour each.



Figure 29. Instrument room at Ingebrigt.

more condensed liquid termed "alkali lignin." The alkaline process would be commercially impractical unless the alkali employed is recovered for re-use. Approximately 280 pounds of sodium sulfate are required to produce one ton of paper. In an efficient recovery system about 190 pounds can be recovered while approximately 90 pounds "make-up" saltcake has to be supplied by the saltcake industry.

Paper industry.

Pulping processes are divided into two categories—chemical and mechanical. These two can be further divided. Chemical pulping includes kraft

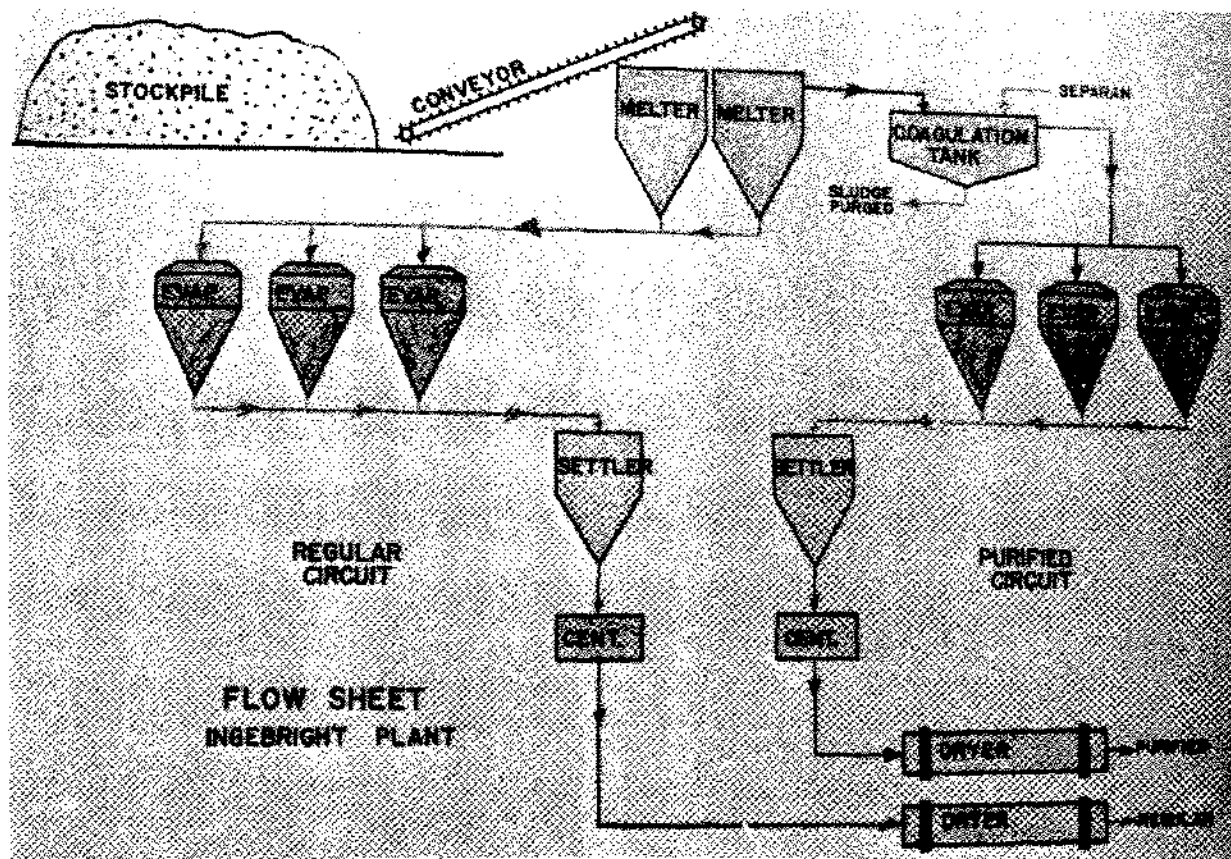


Figure 30. Flow sheet of the Ingebrigt plant. Evap.—submerged combustion elevator, Cent.—centrifuge.

(Na_2SO_4), soda, sulfite, bisulfite, and magnefite processes. In the chemical pulping processes the kraft pulping and the sulfite pulping process are the most important ones today.

In the mechanical pulping process the wood is ground into fibres and only zinc hydrox-sulfite manufactured from zinc dust and sulphur dioxides is used for bleaching.

The sulfite pulping has two advantages, a slightly higher yield and a greater brightness. However, the detrimental disadvantage of the sulfite process is the absence of a chemical recovery system. The spent cooking chemicals and dissolved lignin from the wood have to be sewerred and represent a large pollution load.

The chemicals in the sulfite process used in the wood digestion are SO_2 and $\text{Ca}(\text{HSO}_3)_2$. The calcium cation can be replaced by ammonia, sodium, or magnesium. When magnesium is used the sulfite process is called the magnefite process. The chemicals used in this process can be recovered thus eliminating pollution besides other advantages over the sulfite process.

The Kraft Pulping Process. The use of sodium sulfate goes back to 1879 when Dahl in Danzig introduced sodium sulfate to replace caustic soda in the soda pulping process. The paper from this new pulp was much stronger than that previously obtained and became known as "kraft" from the German word "strong."

The advantages of the kraft pulping process over the sulfite process are:

1. Recovery and re-use of the chemicals
2. Reducing the pollution load
3. Incineration of lignin in the recovery boiler yields approximately 50 per cent steam used in the mill
4. Stronger paper
5. Larger variety of wood species usable

Chemical Recovery. The chemical recovery will be discussed in brief (Fig. 31). When the digestion is completed, the pulp is separated in a washing process from the black liquor. The latter contains approximately 18 per cent solids, chemicals, and

KRAFT PULPING

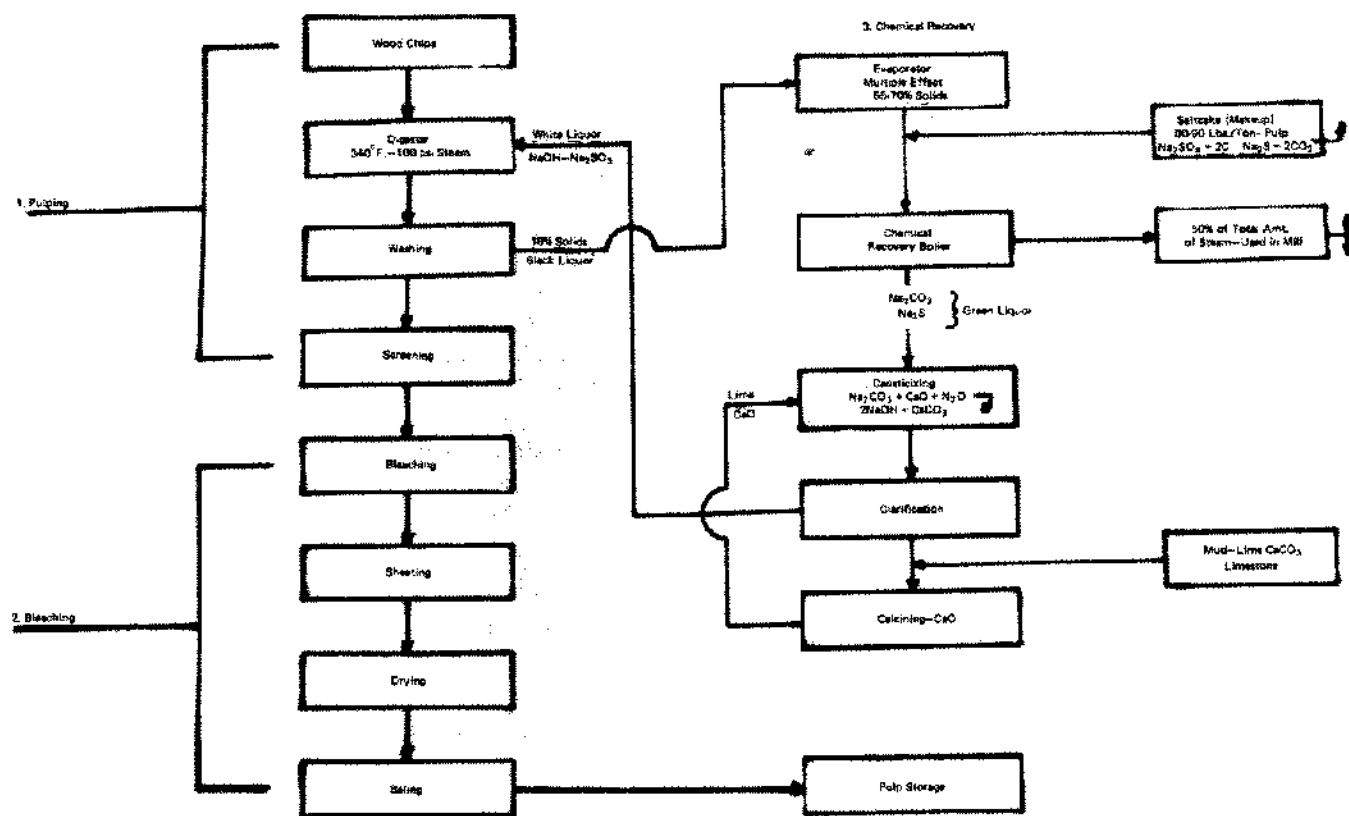


Figure 31. Flow sheet of recovery cycle in a Kraft pulp mill.



Figure 32. Brine pump in a Texas sodium sulfate deposit. Ozark-Mahoning Co., Monahans, Texas.



Figure 33. Brine pipe lines at Searles Lake with town of Trona. American Potash and Chemical Co.

the lignin separated from the cellulose fibres. The solids are concentrated mostly in multiple effect evaporators to approximately 70 per cent. The concentrated black liquor is incinerated in the chemical recovery boiler. The steam generated makes approximately 50 per cent of a mill's steam requirements.

The "make-up" saltcake is introduced here in the process. The chemicals fuse into a smelt of sodium carbonate (Na_2CO_3). This smelt which also contains Na_2S is leached in water and is then called "Green Liquor." The green liquor is causticized with lime as follows:



The CaCO_3 called lime mud is recovered from the caustic solution and recalcined with make-up limestone to CaO for re-use.

In the sodium cycle "make-up" saltcake is added to the black liquor prior to entering the recovery boiler to provide the elements sodium and sulphur. In a reducing atmosphere in the furnace sodium sulfate is reduced by carbon as follows:



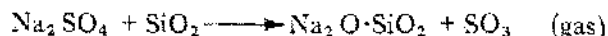
Glass industry.

Before the end of the 19th century the advantages of sulfate addition were known to glass makers. In the voluminous literature of sulfate in the glass industry it becomes apparent that many theories for the role of sulfate in the glass manufacture were brought forward. Complete agreement is still lacking. Rolf Brueckner, Max Plank Institute, Wuerzburg, Germany, brought forward a concept which was reviewed by a FMC research group implementing the hot stage microscope (Figs. 9 & 10). Accordingly, sodium sulfate acts in three stages on the silica melt. At approximately 1900°F Na_2SO_4 is almost completely insoluble in the glass and collects at all melt-solid or melt-gas interfaces. Because of the presence of the fluid sulfate liquid the dissolution of the solid batch particles proceeds rapidly and gas bubbles are expelled.

Above 2400°F the Na_2SO_4 decomposes, upsets the interfacial tension between the two liquid phases, releasing energy which results in a vigorous convective motion at all interfaces in the glass melt. This increases the mixing effect, dissolution of solid particles and expulsion of gas bubbles.

At approximately 2650°F the partial pressure of the decomposition products of Na_2SO_4 reaches atmospheric pressure and a new generation of bubbles develops in the glass. These bubbles help to homogenize the melt. Sodium sulfate reacts di-

rectly with silica at glass melting temperatures according to the following known reaction:



(or $\text{SO}_2 + 1/2\text{O}_2$)

The sodium sulfate has a "surfactant" function. In a sulfate free melt the movement of bubbles is extremely slow and sluggish. In a sulfate containing melt the bubble formation and movement is rapid and vigorous, similar to the classical experiment dropping a piece of camphor into water.

Quantitative measurement of melting rate of a standard soda-lime glass composition as a function of Na_2SO_4 content of the batch, illustrates the remarkable ability of saltcake to increase the melting rate.

Standard Soda-Lime Glass Composition

Silica sand	59%
Limestone	19.10%
Soda Ash	21.30%
Na_2SO_4	.60%

This averages approximately 20 pounds of Na_2SO_4 per one ton of sand.

Detergent industry.

The detergent industry receives its major portion of Na_2SO_4 from the rayon manufacturers. It is used in powdered and spray-dried synthetic detergent compositions to ensure freedom from caking. Sodium sulfate acts as a conditioner and as a "builder" to improve the effectiveness of the organic surfactant.

Animal feed industry.

The main purpose of sodium sulfate in the animal feed industry is to act as a laxative.

MARKETING OF SODIUM SULFATE

Use Distribution

U.S.A.	Kraft Pulping	74%
	Detergent Industry	16%
	Glass Industry & Others	10%
	(Taylor, 1931)	
Canada	Kraft Pulping	95%
	Glass Industry	1.41%
	Detergent Industry	1.99%
	Other	1.70%

(Tomkins, 1954)

Production of Sodium Sulfate

<i>U.S.A. Producers</i>	<i>Source</i>	<i>Capacity</i>
American Potash	Natural	250,000
Ozark Mahoning	Natural	200,000
Stauffer	Natural	200,000
<i>By-Product</i>		
American Enca	Rayon or Cellophane	56,000
Beanuit	Rayon or Cellophane	42,000
FMC	Rayon or Cellophane	275,000
Industrial Rayon	Rayon or Cellophane	36,000
Climax Chemical	Mannheim or Hargreaves Furnace	35,000
Du Pont	Mannheim or Hargreaves Furnace	30,000
Hercules	Mannheim or Hargreaves Furnace	25,000
Morton Chemical	Mannheim or Hargreaves Furnace	120,000
Allied	Bichromate	45,000
Diamond Shamrock	Bichromate	50,000
Hercules	Bichromate	see above
American Cynamid	Others from spent caustic	13,000
Huber	wash and petroleum operations	8,000
Koppers		15,000
Lithium Corp.		15,000
Monsanto		35,000
Stauffer		see above
U.S. Borax		30,000
Miscellaneous		25,000
		<u>1,505,000</u>

(Taylor, 1931)

Canada - Production 1958 173,000 tons
 - Production 1968 469,000 tons

<i>Canadian Producers</i>	<i>Plant Location</i>	<i>Source Lake</i>	<i>Capacity T/yr.</i>
Sodium Sulfate (Sask.) Ltd.	Alsask, Sask.	Alsask	50,000
Francana Minerals	Cabri, Sask.	Snakehole	100,000
Midwest Chemicals	Palo, Sask.	Horseshoe	100,000
Saskatchewan Minerals	Chaplin, Sask.	Chaplin	150,000
	Bishopric, Sask.	Frederick	70,000
	Fox Valley, Sask.	Ingebrigt	150,000
Sybouts Sodium Sulfate	Gladmar, Sask.	Sybouts	50,000
Alberta Sodium Sulfate	Provost, Alta.	Metiskow	100,000
(scheduled to come on stream in May 1969)			
			<u>630,000</u>

(Tompkins, 1954)

*Import/Export**U.S.A.*

Import

Approximately 286,000 T/yr.—1967

Export

Approximately 50,000 T/yr.

Canada

Import

Approximately 30,000 T/yr.—1967

Export

Approximately 123,000 T/yr.—1967

Demand

1967

1,650,000 tons

1968

1,700,000 tons

1972

1,900,000 tons (estimated)

Growth

1957—1967

2.8% per year U.S.

Estimated consumption in Canada 1972

500,000 T/yr.

Productive capacity in Canada 1972

700,000 T/yr.

(Taylor, 1931 and
Tomkins, 1954)

The production of sodium sulfate from natural deposits of Western Canada has advanced from early plant capacities of 50 tons per day to 600 tons per day. Quality has improved from a purity of 90 per cent to 95 per cent with a gray color to a purity up to 99.77 per cent and a white color acceptable to the glass and the detergent industries.

The product can compete successfully against that produced as a by-product from acid manufacture.

Increased production capacity of the Saskatchewan sodium sulfate industry is expected to meet the demands of the expanding pulp and paper industry.



Figure 34. Brine pump at Laguna del Ray, Mexico.



Figure 35. Ingebrigt plant.

COMPOSITION OF SODIUM SULFATE FROM NATURAL DEPOSITS OF THE PRAIRIES

Pure Glauber's Salt Mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$		Ave. Lake Bed Composition Glauber's Containing Insolubles	Brine Pumped into Crystallization Pond	Glauber's Salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) re-deposited during Fractional Crystallization	Dilute Brine After Precipitation Back to Lake	Anhydrous Sodium Sulfate Thenardite Na_2SO_4 After Dehydration
%		%	%	%	%	%
44.1	Insolubles	15.78	1.24	.37	2.83	0.35
	CaSO_4	2.51	0.13	.01	.36	0.01
	MgSO_4	1.15	9.27	.05	20.02	0.02
	Na_2CO_3	Nil	.26	.03	.71	0.00
	NaHCO_3	0.42	.45	.15	.13	0.10
Crystal Bound H_2O 55.9	NaCl	.77	6.20	.07	14.80	0.05
	Na_2SO_4	79.37	82.45	99.32	61.15	99.47
		#-93	#C-14	#C-13	#C-107	#1-3 (Lab. Ref.)

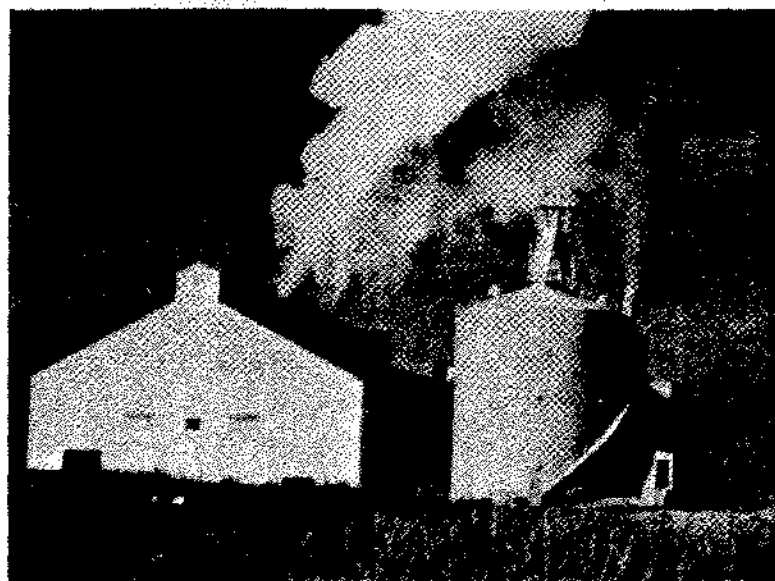


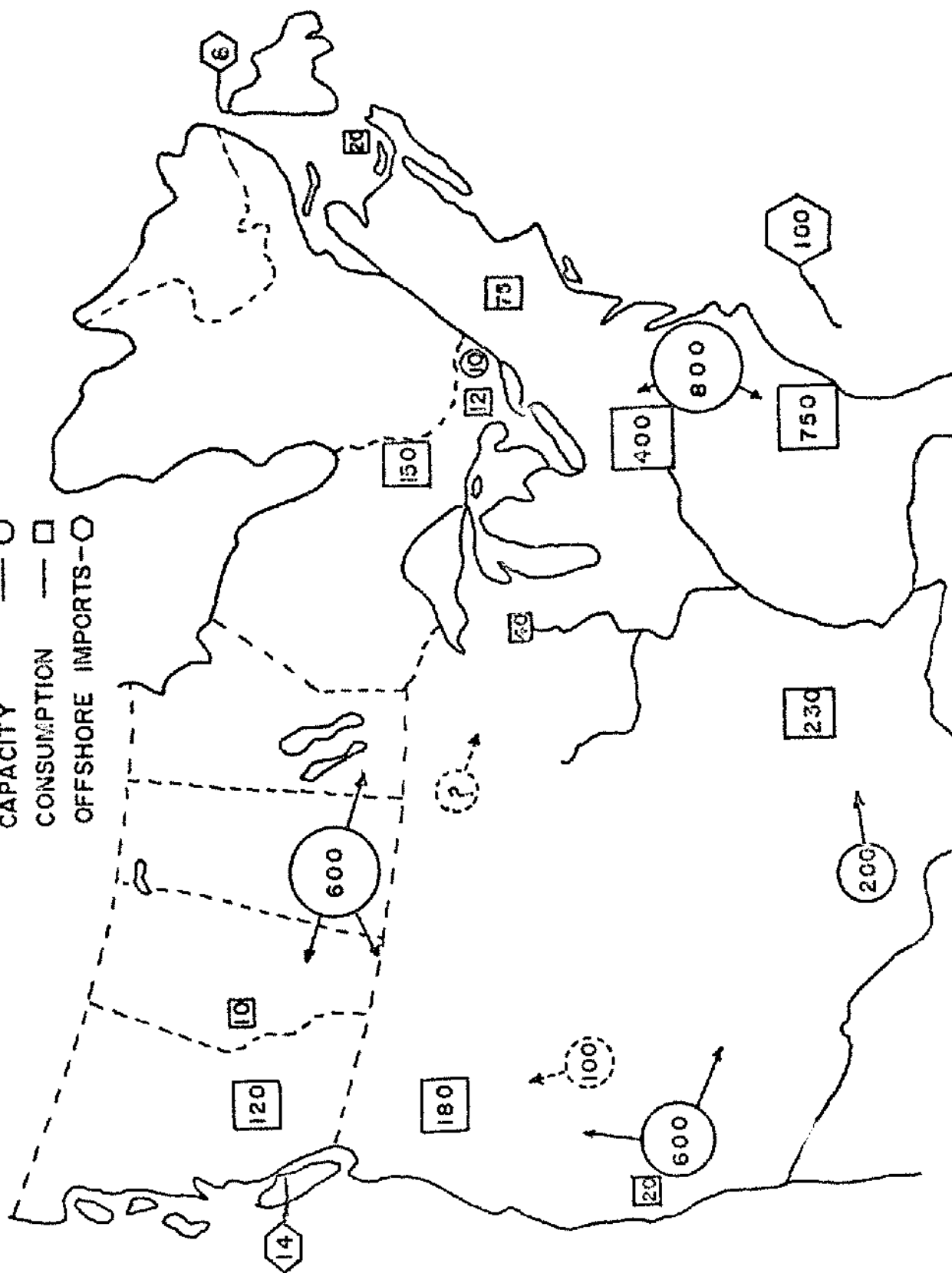
Figure 36. Chaplin plant.

SODIUM SULPHATE—1000 Tons.

CAPACITY —○

CONSUMPTION —□

OFFSHORE IMPORTS—◇



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