Submerged Combustion Process for Evaporated Salt

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ABSTRACT

This paper explains the process of evaporating Salt by submerged combustion, also the reasons to the decision of installing this new type of plant for evaporated salt and the results of five years of experience.

INTRODUCTION

About 20 years ago, our company, Industria del Alcali was formed with the purpose of investigating the possibilities of establishing a business to produce sodium carbonate and other basic chemicals. In order to produce these chemicals, we needed sodium chloride and calcium carbonate as raw materials. We hoped the deposits would be close to each other and not far from the consuming centers.

For this purpose, geological investigations were made all over Mexico. By 1959 these investigations were concentrated near Monterrey (about 140 miles south of Laredo, Tex). The project required the installation of a plant for producing soda ash by the Solvay Process. We contacted the Allied Chemical Corporation to obtain technical assistance in the construction and operation of the plant and also to consider the manufacture of other products such as sodium chloride, sodium bicarbonate, ammonium bicarbonate, calcium chloride and caustic soda.

Alcali assisted us in the geological investigations and in the market research of the products. A work program was developed to assure that the total amount of raw materials would enable us to operate for over a hundred years.

GEOLOGY AND ORIGIN OF SALT DEPOSITS IN NORTHEAST MEXICO

The region around Monterrey has a geologic section which includes formations that range from Recent to Jurassic in age.

In the lower Cretaceous we have the following stratigraphy:

Cuesta del Cura.
Aurora.
La Pena.
Cupido.
Taraises.

The Upper Jurassic section includes the Casita Shale, Zuloaga Limestone, Minas Viejas Gypsum and the Lovann Salt.

The Minas Viejas is a gypsum and anhydrite section about 660 meters thick. It contains white to pink gypsum and anhydrite with some sulphur. This gypsum is only exposed within the very center of the axis of the anticlines in the area.

The Lovann Salt is a sequence of evaporites with redbeds, gypsum, potassium minerals and salt. The underlying sequence is a series of limestones which are probably Paleozoic in age.

In the area of the Sierra Madre Mountains, the section where salt should occur crops out as a sequence of redbeds. This region has been a large sedimentary basin in the past. During Jurassic time this basin received evaporite sequences. In post Cretaceous time, the area was intensely folded.

The basin was not folded as extensively.

The sequence of deposition is similar for a large area of Mexico.

After these studies, we investigated more closely the Sierra del Fraile anticline, because of its nearness to Monterrey.

The Cretaceous and upper Jurassic sediments were deposited in a basin referred to by Humphrey as the Sabinas Gulf. The basin lies between the Peninsula of Coahuila and a main land mass at the eastern side of Mexico, which is called Peninsula Tamaulipas.

Anticlines such as Sierra del Fraile are located in what has been called the Coahuila Ridge and Basin Province. These are part of a north trending orogenic belt.

Little was known about the Jurassic sequence within this area. It was hoped that the salt depositional basin was large enough to extend to Fraile so that salt sequences rather than redbeds would be encountered in the Upper Jurassic section.

An exploratory hole was drilled on the axis of the anticline to 1,500 meters without Fraile. We hit the salt at 660 meters, but continued drilling to 1,500 meters without completely penetrating the salt bed.

We continued drilling explanatory holes with the purpose of determining the limits of the salt bed and in every hole we encountered salt at a depth of 660 meters and with a minimum thickness of 1,000 meters.

In another anticline about 40 km. north of Fraile an exploratory oil well penetrated over 3,000 meters of salt.

After the exploration we established that the salt bed was 5,000 meters long and 1,000 meters wide. This volume indicates that 5 billion cubic meters of salt is available.

We proceeded to drill two production brine wells for our soda ash operation.

DECISION TO INSTALL A SALT PLANT

In order to develop the cavities of our brine wells to assure an almost saturated brine for the soda ash operation we had to pump about 100,000 metric tons of salt from the wells. We could not dispose of this brine into the nearby river because of pollution.

In order to solve this problem we installed a plant to produce 30,000 tons of salt per year.

To determine the method to use for production we made an economic study which considered four alternatives:

(a) Conventional evaporation plant located at the brine wells.

(b) Conventional evaporation plant located at the soda ash plant site and readily integrable with a soda operation.

(c) Solar salt production located at the site of the projected soda ash plant waste beds.

(d) Submerged combustion salt plant located at the soda ash plant site.

With further information on soil porosity, we considered the solar salt to be impractical because of the high capital investment needed to provide adequately impermeable beds. Further, the relatively poor salt quality, and the variability of production capabilities due to weather conditions ruled out the solar salt ponds.

Although the initial capital requirements were less, we did not find it was advisable to locate an evaporation salt plant at the brine wells because it could realize few of the eventual benefits of integration with the soda ash operation. In comparing the two remaining cases, the initial capital requirements and operating costs for submerged combustion facilities located at the soda ash plant site were slightly less than these applicable to a conventional evaporation plant. The short time required for installation, for start-up, and operation along with the minimum initial investment required, outweighed the probably optimum long-term economy of an evaporation salt plant.

The Ozark-Mahoning Co. of Tulsa, Oaklahoma provided technical assistance and know-how, and a design which enabled us to develop a package salt plant with an annual capacity of 30,000 metric tons of salt.

BRINE PURIFICATION

Crude brine solution, saturated with respect to sodium chloride and containing dissolved calcium sulfate, enters the plant from the brine wells.

The crude brine enters the brine purification section where liquid soda ash is added along with milk of lime to the mixing tank. Subsequently, the mixture is passed thru four reaction tanks and the settler.

Control samples are taken from the discharge of the third reaction tank and are carefully analyzed by the operator so that he can adjust the reagents.

Completion of the reactions is signified by the appearance of a "break" in the reaction tanks, where the turbid solution takes on the resemblance of curdled milk.

The reaction tanks are agitated sufficiently to keep the major portion of the insoluble solids in suspension, but not so great as to cause mud particles to grow.

Because of scale formation in the center tubes and the accumulation of unreacted soda and other heavy muds in the reaction tanks, periodic cleaning is necessary.

If these tanks are not cleaned when needed, experience has shown that the settling quality of the muddy brine is impaired causing a sub-standard quality brine.

The turbid brine leaving the last reaction tank is distributed to compartments with separators to provide streamlines of flow. Then in each compartment the brine meets a wooden baffle that prevents the effect of turbulence. Further, its direction is changed to permit a combination of upward as well as horizontal flow across the settler to the outlet side. The level is controlled by wiers.

Mud levels in the settler are maintained and controlled by taking depth samples.

Maintenance of the heavier mud concentration level at 5 to 6 feet from the surface has been found best for both purified brine quality and thickness of the discharged muds. The mud draw is increased or decreased to hold this level.

Mud is withdrawn by a drag and ribbon conveyor system and sent to the sewer by a pump.

About the only controls in settling are rate of operation, mud level and consistency of the mud draw. The clarified brine goes to a pump and then to the purified brine storage. The turbidity of this brine should not exceed 15 ppm.

SUBMERGED COMBUSTION PROCESS

Purified brine is pumped to the submerged combustion plant where the volume of entering brine is metered and held in a small storage tank. From storage, the brine is pumped to the evaporators where water is removed by submerged combustion techniques.

Submerged combustion evaporation involves the burning of a natural gas—air mixture under the surface of the evaporating liquid.

The hot combustion gases are released into the brine where bubbles are in intimate contact with the liquid. These gases pass up through the brine evaporating water and are vented to the stack. Where water is evaporated from the saturated brine, sodium chloride and a small content of impurities crystallize. Because of a large concentration gradient between the compounds in solution, the impurities form much smaller crystals than the sodium chloride. This difference in crystal size can then be used to improve the salt quality by differential settling.

When a particle settles through a fluid, it soon attains a maximum settling velocity, which is a function of the fluid properties and the particle size and density. Thus, when two similar particles settle through the same fluid, the larger will obtain a higher velocity, and sink more rapidly. To take advantage of this fact, the salt evaporators have been designed with the brine feed and salt slurry draw at the bottom. The brine feed volume is greater than the slurry volume, resulting in a net upward flow of liquid in the bottom of the evaporator.

This allows the larger NaCl crystals to settle out and be removed, while the smaller impurities crystals remain in suspension because their terminal velocity is less than the net upward flow rate. The impurities may then be purged from the body of the evaporator.

There are two evaporators, each designed and built by Ozark-Mahoning, to evaporate 5.16 MT/hr. of water from 8.02 MT/hr. of brine, with a purge rate of about 1.0 MT/hr.

Each evaporator consists of a conical bottom tank 10′6″ in diameter with a side wall height of 4′ and a maximum capacity of 17.5 M^3.

Inside the tank is a 15″ diameter O-M submerged combustion burner fabricated of inconel. A mixture of air and natural gas is fed to the burner to release 17,000,000 BTU/hr. The burner is normally ignited with an igniter rod and glow plug and equipped with a fireye scanner system to automatically stop gas flow in event of a flameout. The flow of air and natural gas is automatically adjustable to about 60% of full flow.

The control of the salt plant is primarily a manual operation with the exception of the combustion gas ratio control system, which is automatic. Proper adjustment of the various evaporator streams is required for steady operation.

There are six streams entering and leaving the evaporators. The feed streams are—the purified brine feed, the combustion mixture and the mother liquor recycle. The three exiting streams are—the slurry draw, the mother liquor purge and the exhaust gases.

The purified brine feed to the evaporators is measured by the brine feed rotameter, and is adjusted to give the desired production rate.

The rate of combustion in the evaporators must also be regulated to maintain production.

The prime control on the combustion system is the air by-pass valve, which is manually adjusted to provide the desired flow rate, which is then read on the ratio control instrument.

The evaporator draw is a slurry consisting of precipitated NaCl in saturated brine. This stream is not directly measured, but a sample taken at the slurry pump outlet should show about 28-30% settled solids.

This flow rate may be adjusted by the slurry pump discharge valve, as the evaporator level requires.

The salt slurry is pumped to a liquid cyclone where it is thickened by removing part of the mother liquor. The liquid cyclone used to thicken the slurry is of porcelain construction with neoprene tubing connections.

This unit removes a portion of mother liquor before the slurry enters the centrifuge and operates with a pressure differential. Under these conditions, all particles larger than 35 microns should be removed from the mother liquor.

The concentrated slurry is then fed to a centrifuge. In the centrifuge, the salt is washed with purified brine and the damp product, containing about 3% moisture, is conveyed directly to the salt dryer. The mother liquor overflow from the liquid cyclone and centrifuge is recycled to the evaporators.

Each evaporator is provided with its own air supply system. This system consists of a blower, an air intake cleaner, a silencer and a snubber.

The system is capable of delivering 5050 M^3/hr. of air to the burners, at a pressure sufficient to overcome the static head in the evaporators.

The mother liquor purge in the evaporators has been greatly diminished, almost 95%, due to the change of feeding the evaporators with purified brine instead of crude brine.

The analysis of the final product coming out of the dryer is 99.9% NaCl and is distributed throughout the country for special customers who need this purity.

USES OF SALT

Most of the salt produced by us is used in the chlorine and caustic soda industry in Monterrey and Mexico City.

Another important use is in coagulating latex for producing synthetic rubber.

Manufacturers of optical bleachers, textile and food coloring anilines also demand a salt of high purity.

It is used extensively for water treatment, cattle salt, canneries, chemical products, etc.

SUMMARY

Our submerged combustion salt plant is now producing 33,000 MT/yr., and we only supply 6% of the total 500,000 MT/yr. Mexican market. We are planning to expand production to 100,000 MT/yr. which is 20% of the actual market. Another 500,000 MT/yr. of salt is consumed as brine by soda ash and chlorine industry.

The salt market in Mexico is rapidly increasing with the growth of the chemical industry and specially of the petro-chemical industry which is a great consumer of chlorine.