The International Recrystallizer Process

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ABSTRACT

The International Recrystallizer is a new process developed by the International Salt Company for production of a high purity evaporited salt from rock salt screen tailings or other forms of relatively impure salt. The process takes advantage of the inverse solubility of rock salt's chief impurity, calcium sulphate, so that brine purification by chemical treatment is eliminated. Other advantages, when compared to more conventional salt evaporating processes, at lower first cost and greatly improved operating economy. A double-effect, 15 ton per hour unit is now in its fourth year of trouble free operation at the Avery Island, Louisiana Mine and Refinery of International Salt Company. The process is readily adaptable to purification of solar salt, the use of vapor recompression in regions where electrical power is cheap, and it can be used for the resaturation and purification of spent Mercury cell brine.

INTRODUCTION

A high purity end-product with lower capital investment and lower operating costs -- these are the major advantages of the International Recrystallizer Process, now nearing the end of its fourth year of operation at the Avery Island, Louisiana Mine and Refinery of the International Salt Company. The purpose of this paper is: (1) to describe the principle and operation of this process, (2) to compare its advantages with conventional salt evaporators and (3) to discuss other possible applications.

The International Recrystallizer Process was developed to transform relatively impure forms of sodium chloride, such as waste rock salt, solar salt or refuse salt, into an evaporated salt of exceptionally high purity. Salt is being produced at Avery Island, with a sodium chloride content in excess of 99.99%. The process has been designed to eliminate many of the disadvantages of more conventional salt evaporating methods. The elimination of these disadvantages has resulted in low operating costs. Before going into the process in detail, it is desirable to review very briefly, the development of salt evaporators in general together with the advantages and disadvantages of the different types.

BRIEF HISTORY OF SALT EVAPORATORS

The first salt evaporators of record were open kettles heated by a direct fire. A number of salt industries grew up in wood producing areas, where waste wood was burned to produce steam which was fed to flat open pans. (1) This was the origin of so-called grainer salt, a coarse type of crystal for which there still exists some demand today. These open pans developed into today's grainer pans, into which steam is fed to coils in the pans and the brine is heated to just below boiling so that a slow surface evaporation takes place and the characteristic coarse, hopper-like crystal of salt is formed. Fortunately, the demand for this type of salt is diminishing, for the grainer process is an expensive and inefficient method for producing salt. Also, the desirable coarser fraction of the crystals is hard to preserve due to their fragile nature.

A major improvement in grainer salt production was the introduction of the Alberger Process around 1910. In this process, a portion of the brine in the grainer pans is recycled to tubular heaters, where the brine is heated and the calcium sulfate in the brine reaches its minimum solubility. Most of the calcium sulfate in the brine is precipitated and then deposited onto a bed of gravel. The brine is then flash cooled in flashers and it becomes undersaturated with respect to calcium sulfate and only pure sodium chloride is precipitated. The advantages of this process are a very pure end-product and a fairly low steam consumption, (around 3, 000 pounds per ton of salt). The disadvantages are a very rapid scale formation in the tubular heat exchangers and a small, more fragile crystal compared with conventional grainer salt. (3)

A single effect vacuum evaporator was first used in the manufacture of salt in 1887, after the principle had been in use for over a half a century in the sugar industry. (2) The first multiple-effect evaporator appeared in 1899, and since then, multiple-effect vacuum evaporators have completely overshadowed open grainer pans in the production of evaporated salt, primarily because of much lower steam consumption per ton of salt produced. In addition, present day capacities would require vast numbers of grainers.

The first type of vacuum evaporator to receive wide popularity was the short-tube-vertical type. Even though this type of salt evaporator was a standard in the industry for most of the first half of this century, its disadvantages were apparent: (1) The low velocities through the tubes resulted in poor heat transfer; (2) velocity distribution in the tubes was uneven; (3) venting of non-condensibles was difficult; (4) the internal propellor and bearing and internal tubes were difficult to maintain. (6)

Because of these disadvantages in the calandria type of evaporator, the next major improvement in salt evaporator design was forthcoming. It had been realized for many years that improved performance in salt evaporation could be achieved by increasing the brine velocity through the tubes. (2) (6) By providing an external pump and external tubular heat exchanger through which the brine could be pumped at higher velocities, higher heat transfer rates were attained and the forced circulation evaporators became the most preferred of all the conventional salt evaporators.

Nevertheless, certain operating problems exist, even in the most modern of forced circulation evaporator installations. Tubular heating surfaces tend to scale thus decreasing heat transfer and capacity; undesirable salts concentrate in the evaporators sometimes affecting crystal formation; expensive chemical treatment of brine is necessary when a salt of high purity is desired; and evaporator equipment is expensive to acquire. (4) The International Recrystallizer Process was developed to eliminate most of these undesirable features found in conventional evaporating processes.

PRINCIPLE OF OPERATION

Before going into a detailed description of the Recrystallizer Process as it is operated at Avery Island, it would be well at this point to examine the general principles of the process. To begin with, it should be made clear that the Recrystallizer Process requires that the raw salt fed into the system be in a solid and preferably finely crushed state. That is to say that salt brine, such as from a well or from the sea, cannot be fed directly into the system without going through a prior stage of crystallization. This is because the water balance of the system is such that there is no net evaporation capacity. The dissolving of the salt and heating of the brine take place simultaneously by the direct injection and condensation of steam into the system. The chief impurity in salt is usually calcium sulfate. This is especially true of rock salt. Calcium sulfate solutions in water and brine have an inverse solubility curve at temperatures above 100° F. The Recrystallizer Process takes advantage of this inverse solubility by heating and dissolving the raw salt in a direct contact heater into which steam is injected and condensed. The salt is previously slurried with a brine from the evaporator so that it can be easily handled in a highly fluid state. Since the heating and dissolving action occurs almost simultaneously, any calcium sulfate that is fed in with the raw salt is prevented from going into solution.

There are three principal zones in the process. (1) The first is the condensing, heating and dissolving zone which we have just examined. (2) The second is the clarification zone where the undissolved impurities, principally calcium sulfate, are separated from the brine by settling and filtration. (3) The third zone is the evaporation, cooling and crystallization zone where the hot clarified brine is flash-cooled to a lower temperature in a vacuum vessel, with a resultant release of vapor to a condenser and the formation of salt crystals both due to the evaporation of water and the cooling of the brine. (While sodium chloride is considered to have a fairly flat solubility curve, there is enough of a decrease in solubility with a drop in temperature to cause about half the crystallization to result from cooling.) Another important feature of this evaporation zone is that the brine becomes undersaturated with respect to calcium sulfate due to the cooling that takes place. Therefore, the resultant salt crystals are virtually free of any impurity, except for small traces occurring on the crystal surface due to small amounts of mother liquor drying on the crystal.

An interesting feature of the condensing, heating and dissolving zone occurs in the direct contact heater. This heater is usually operated at atmospheric pressure and the steam being fed to it is essentially at atmospheric by the time it reaches the heater itself. The condensing action of the steam causes the brine to be heated up to slightly less than the boiling point of a saturated solution of brine, which is 226° F. This is close to 14° above the temperature of the condensing steam. In this heater, it is the vapor pressure that is controlling. The brine is heated to such a temperature that the vapor pressure of the brine is almost equal to the vapor pressure of the condensing steam.

The use of this direct contact method of heating results in a theoretrical steam consumption of 3,000 pounds of steam per ton of salt in a single effect unit. A double effect unit can approach 1,900 pounds of steam per ton of salt and the steam consumption of a triple effect unit is calculated to be 1,400 pounds of steam per ton of salt. In multiple-effect designs, vapor coming from all but the last effect evaporator is recycled back to low and intermediate stage direct contract heaters.

PRACTICAL DEVELOPMENT OF THE PROCESS

In the late 1940's at the Watkins Glen, New York Refinery of the International Salt Company, the first pilot plant model of the Recrystallizer was constructed and operated. A great deal was learned about the process from this initial pilot plant and even though a full scale installation was not immediately forthcoming, without the experience gained on this early model, much of the subsequent work would have been made a great deal more difficult. The most important accomplishment with this first pilot plant was that it proved the theoretrical aspects of the process. Yet to be proven, however, was whether or not the process could be designed and constructed so as to insure smooth and trouble-free operation.

It was for this purpose that a second and much more elaborate pilot plant was designed, constructed and placed into operation in 1957 at Watkins Glen. This double-effect, one ton per hour unit was operated successfully for several months, with only minor design changes necessary. It was as a result of the excellent operation of this second pilot plant that a full scale unit was constructed at Avery Island, Louisiana.

THE RECRYSTALLIZER OPERATION AT AVERY ISLAND

A problem common to many rock salt mining operations is that of excessive fines production. Because of superior handling and dissolving characteristics, the coarser grades of rock salt have become so much in demand, that the tailings from the screening operation are, to a large degree, a waste product, even though these fines are usually purer than the coarser grades. At some salt mining operations, this waste has exceeded 20% of the total production. Control of blasting and salt handling has for the most part reduced these amounts of fines to a minimum. Nevertheless, the problem of fines disposal or utilization still exists.

Several means of coping with this problem of fines have been developed. At one salt mine, the fines are compressed into briquets and then reacted with sulphuric acid to produce hydrochloric acid and salt cake. Other mines have installed compaction devices to produce a coarser and more saleable product. Still other mines have installed evaporators, and after dissolving and treatment steps, the resulting brine is fed to the evaporators where evaporated salt is produced.

This was the step taken at the Avery Island, Louisiana Mine of International Salt Company in 1932, when two cast iron calandria type evaporators were installed.

The waste rock salt was dissolved in a large pond and the resulting brine, after purification with lime and soda ash treatment, was fed to the evaporators. The steam consumption was about 4,500 pounds per ton of salt. At Avery Island, 15% of the rock salt produced passes through a 10 mesh screen and this salt represented a waste product until this evaporating plant was installed. The major disadvantages of this process were (1) the high cost of chemical brine treatment; (2) high steam consumption per ton of salt; (3) product contamination from the cast iron evaporators; (4) low capacity (averaging about 10 tons per hour); (5) the necessity of frequent soak outs to dissolve salt buildup inside the evaporators; (6) $CaSO_4$ buildup in the tubes of the evaporators requiring frequent acidizing.

Because of the disadvantages of the existing evaporating plant and because additional production capacity was needed, a 15 T.P.H. double-effect International Recrystallizer was installed at Avery Island and placed on stream in August of 1958. It is now completing its fourth year of operation. The steam consumption has been approximately 2,100 pounds per ton of salt. This is equivalent to the steam consumption of a quadruple-effect forced circulation evaporator.

The International Recrystallizer Process at Avery Island operates as follows: Mine fine rock salt is fed at a controlled rate into a slurrying tank, which also receives recycled mother liquor from and at the temperature of the second effect evaporator which operates at a boiling point of about 130° F. The resulting slurry of fine rock salt and brine is then pumped to a direct contact heater, referred to as the low temperature heater. Vapor coming off the first effect evaporator, which is boiling at 175° F., is piped to this low temperature heater. The temperature of the vapor is about 163° F. The cooler slurry, cascading down over the internal baffles in the heater causes the vapor to condense which heats the slurry up to a temperature within 5° F. of that of the first effect boiling temperature. Also, a portion of the rock salt in the slurry is dissolved by the condensate that has mixed with the brine. The resulting rock salt slurry, at 170° F., is then pumped to a second direct contact heater, called the high temperature heater. Into this vessel is injected exhaust steam from a turbo-generator. This steam leaves the turbine at 3 pounds per square inch gage and is fed at a controlled rate into the heater in order to keep the pressure in the heater at just a fraction over atmospheric pressure. This steam condenses in the heater and raises the temperature of the brine to approximately 222° F. which is 4° F. below the theoretical boiling point of fully saturated brine, at atmospheric pressure. The combined effect of heating and dilution causes the remainder of the rock salt to dissolve.

This hot brine is then pumped into a saturator vessel. Any excess rock salt that might be fed in momentarily is deposited in this saturator against the time when an under feed of rock salt might occur, thus assuring saturated brine at all times. Also deposited in this saturator is the coarse portion of the anhydrite crystals from the rock salt. From the saturator, the brine is fed to a large settling vessel where the major portion of the anhydrite is settled out. The overflow from this settler is then pumped to a set of six pressure type, anthrafilt filters. These filters remove the last traces of suspended anhydrite from the brine and, in addition, remove any suspended iron particles that may have been picked up from the carbon steel vessels between the feed tank and the thickener.

Then, at a manually controlled flow rate, the brine, which is fully saturated, completely clarified and at 220° F., is fed into the first effect evaporator. This evaporator is similar to a forced circulation evaporator, with its external axial flow circulating pump, tangential inlet and swirl breaker to prevent a vortex from forming in the suction line of the circulating pump. The major difference is the absence of a tubular heat exchanger in the circulating piping.

As previously mentioned, the boiling point in the first effect evaporator is 175° F. The hot (220° F.) clarified brine from the filter is injected at the suction side of the circulating pump. The resulting mixture of circulating magma and hot brine is then pumped up and into the evaporating chamber where flash cooling occurs. The inlet to the evaporator itself is kept sufficiently submerged to prevent boiling of the mixture until it has entered the main body of the evaporator.

The purpose of feeding the hot brine from the filters into a large volume of recirculating magma is to reduce the temperature elevation of the brine entering the evaporator body. The flash range is reduced to about 5° F., thus permitting control of the resultant supersaturation and of the particle size of the final product.

Salt is produced in this evaporator both due to the evaporation and due to the cooling of the brine. This produced salt settles by gravity down an elutriating leg against a rising current of brine. A certain amount of classification occurs in this leg and the coarser portion of crystals are removed from the evaporator periodically.

A portion of the circulating magma in the first effect evaporator system is continuously pumped into a clarifying vessel in which the magma is thickened 2 to 3 times and the resulting clarified brine (or mother liquor) is piped off and pumped to the second effect evaporator. The thickened magma flows by gravity out of the bottom of the settler and back into the first effect circulating system.

The main purpose of this settler is to permit increasing magma density in the first effect evaporator beyond the normal "make." Without this settler, it would be impossible to obtain a magma density of over 1-2% salt. With the settler, it is possible to achieve all ranges of magma density and control of crystal size is the result. The magma density is usually carried between 20 and 30%, with the higher values yielding a coarser product.

Just as clarified brine at 220° F. is fed into the suction side of the first effect circulating pump, the clarified mother liquor coming from the first effect settler at 175° F. is pumped to the second effect where flash cooling occurs.

The resulting crystals of salt gravitate down an elutriating leg against a classifying current of brine and are withdrawn with the crystals from the first effect evaporator. The vapor from the second effect evaporator goes to a barometric condenser where it is condensed and sewered. A two stage jet-type steam ejector is used to remove non-condensible gases from the evaporators. A second settler permits magma density control in the second effect. It also permits a clarified brine to be returned to the feed tank where additional rock salt is slurried.

A small amount of dissolved calcium sulfate reaches the first effect evaporator from the filters. Actually, the brine is saturated with respect to $CaSO_4$ at 220° F.

Due to the inverse solubility curve of calcium sulfate, the brine, in cooling as it enters the first effect and then the second effect, becomes undersaturated with respect to calcium sulfate, and the resulting sodium chloride crystals are almost entirely free of this impurity, except for minute traces of brine that become trapped in the crystals during the crystallization process. The small traces of calcium sulfate that appear in the finished product are actually due to mother liquor that has dried on the surface of the individual salt crystals. By washing the filter cake just prior to the drying process, the purity of the final product can be increased to where only a trace of calcium sulfate is measurable. A final product with less than 5 P. P. M. of calcium sulfate can be produced in this manner.

The slurry of crystallized salt and brine being discharged from the elutriating legs of the two evaporators is pumped onto a rotating filter, constructed of 316 stainless steel. A cake of about 1 inch in thickness is deposited on the filter screen and the brine is immediately dewatered from the salt. The rotating screen carries the cake into a drying zone where gas heated hot air at 380° F. is passed through the cake. This air is removed by means of a steam driven centrifugal exhauster. After passing through the drying zone, the salt cake is scraped off the filter and is fed into kiln-type cooler where the salt is cooled from 220° F. to 130° F. by a counter-current flow of air. From the cooler the salt is conveyed to a screening process where it is separated into 3 commercial grades.

PROPER INSTRUMENTATION IS IMPORTANT

A very important phase of the Recrystallizer design was the application of automatic controls. The high flows (1600 gpm) through the system and the need for close liquid level control dictated that an accurate and reliable set of controls be installed. Automatic level controls have been installed in the feed tank, both low and high temperature heaters, the thickener and both evaporators. Purgeless sensing elements are used to eliminate water addition to the system. A remotely controlled gravimetric feeder is used to feed the fine rock salt into the feed tank and a series of six magnetic flow meters balances the amount of brine going through each filter. It is at this point that the total flow through the system is controlled. A radio-active gage measures the specific gravity of the brine leaving the saturator because undersaturation impairs operating efficiency. A temperature recorder continuously shows temperatures at key points in the system.

The problem of corrosion and the resulting contamination of the final product with particles of iron oxide have been eliminated by the use of monel evaporators. Carbon steel vessels in the section between the feed tanks and brine filters are being used successfully and these are being cathodically protected. An exception is the high temperature heater which is a monel vessel.

Because of the mild climatic conditions at Avery Island, all of the major equipment was installed outdoors. Suitable insulation covers the vessels and piping to minimize heat loss. An air conditioned control room houses the instrumentation.

Removal of insolubles separated from the brine in the clarification zone is accomplished as follows: (1) the coarse portion of the insolubles which remains in the saturator is removed by blow down once per week; (2) the middle portion of the insoluble matter is settled out in the larger settling vessel and this is blown down upon signal from a rotating rake mechanism; (3) the fine insoluble matter taken out at the filters is backwashed with clarified brine from the thickener every two weeks. This backwash is pumped into the thickener, where the insolubles are removed with the medium fraction of insolubles at the thickener underflow.

The principal advantages of the International Recrystallizer are as follows:

1. Low steam consumption per ton of salt: The theoretical steam consumption per ton of salt for a double effect is 1900 pounds per ton. In actual practice at Avery Island, this consumption has been running closer to 2100 pounds. This is less than half the steam consumption of the double effect calandria evaporators which the Recrystallizer replaced. In addition, this low steam consumption compares favorably with quadruple effect forced circulation evaporators, which consume about 2200 pounds of steam per ton of salt produced. The theroretical steam consumption of a triple effect Recrystallizer is 1400 pounds per ton against 2600 pounds per ton in a conventional triple effect.

   The main reason for the low steam consumption possible with the Recrystallizer is that there is a maximum use made of the temperature drop available. In conventional evaporators, there is a loss of effective temperature levels due to the boiling point rise in each effect.

2. High purity end product with no chemical treatment necessary: Because of the inverse solubility of $CaSO_4$, the hot brine passing through the filters to the first effect is extremely low in dissolved $CaSO_4$. After the brine is cooled in the evaporators, it becomes undersaturated in respect to $CaSO_4$. Therefore, the only $CaSO_4$ removed with the final product is the small amount carried out in the mother liquor and dried on the crystals. Salt produced in the Avery Recrystallizer has constantly exceeded 99.99%. By washing at the filter, $Ca\ SO_4$ content can be reduced to 5 P. P. M.

3. Low initial cost: Because tubular heat exchangers are not necessary, a major cost item found in conventional evaporators has been eliminated. In addition, for a given steam consumption, fewer effects are required.

Other applications have been envisioned for the International Recrystallizer. For example, in regions where there is a relatively cheap source of mechanical power, the process is readily adaptable to thermo-recompression of the vapor leaving the last effect. This recompressed vapor is then returned to the high temperature heater.

In order to keep the size and cost of the compressor to a minimum, the high temperature heater could be operated at higher pressures and temperatures permitting a lower vacuum. The resulting decrease in specific volume of the vapor to be compressed would result in major savings because of smaller compressor requirements. Of course, all equipment from the high temperature heater to the first effect evaporator would have to be pressurized.

The Recrystallizer is ideally suited to the refining of solar salt. A major impurity in solar salt is Mg Cl_2 and recent pilot plant tests on solar salt have yielded a final product containing 13 p.p.m. of calcium (as calcium chloride), no magnesium and no sulfate. These tests were conducted without any chemical treatment.

A third application which fits in nicely with the International Recrystallizer is in connection with the electro-chemical decomposition of salt in solution such as in a mercury cell. The spent liquor from a mercury cell is 85% saturated, and fully saturated brine relatively free of calcium sulfate is required for cell feed. The Recrystallizer can be used for providing a saturated, high purity brine by recycling of the dilute brine from the cells through a feed tank in which impure make-up salt is fed. The brine is immediately strengthened and then processed as in a conventional Recrystallizer. A portion of the spent liquor is by-passed around the Recrystallizer and is mixed with the slurry of refined salt and pure brine withdrawn from the evaporators. This is then fed back to the cell.

International Salt Company has concluded an exclusive arrangement with W. L. Badger Associates, Inc., of Ann Arbor, Michigan, to handle all engineering and licensing matters on the International Recrystallizer Process for purification of sodium chloride and other chemicals. W. L. Badger Associates, Inc., has in turn concluded arrangements with Escher Wyss of Zurich, Switzerland, to market and build International Recrystallizers in all countries of the world outside of the United States and Canada. Similar arrangements have been made with the Swenson Evaporator Division of the Whiting Corporation for the United States and Canada.

SUMMARY

The International Recrystallizer Process has taken its place along side more conventional evaporation processes for the manufacture of refined sodium chloride. Many of the difficulties encountered in the conventional processes have been eliminated.

The successful operation of a double effect unit at Avery Island, Louisiana, for almost four years has proven the reliability and economy of the process. A refined salt of extremely high purity with only a trace of Calcium Sulfate has been produced at an average steam consumption of a little over 2000 pounds of steam per ton of salt. The process is especially adaptable to installations where a solid waste salt, such as fines from a mining operation, is available.

New applications of the process are envisioned, especially those relating to the use of solar salt, thermo-compression, and the resaturating and purification of spent mercury cell brine.

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