

RECRYSTALLIZATION PROCESS FOR THE UPGRADING OF ROCK- AND SOLAR SALTS

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ABSTRACT

The recrystallization process is a known, but until now little used process in salt plants. It can be applied in cases, where the raw material is present in the solid form (rock- and solar salt). Compared to other vacuum salt processes, recrystallization requires lower specific energy consumption (steam, electricity). A further significant characteristic is the high vacuum salt quality, which can be achieved almost without the addition of chemicals. Raw salts with a large portion of natural impurities, can be economically converted into a high-purity product.

The recrystallization process belongs to the category of the adiabatic flash evaporation processes. A hot, saturated brine will be led into several flash crystallizers working on different pressure levels. Supersaturation is achieved in the vacuum crystallizers by simultaneous evaporation and adiabatic cooling of the brine feed, and subsequently the production of crystallized salt will start.

1. INTRODUCTION

There is salt in the nature in crystalline deposits (rock salt, solar salt in salt lakes) and in dissolved form (sea water, salt lakes, natural brine). Depending on the salt source or the used salt production technology, the concentration of natural impurities in the salt is very different. Basically, they can be divided into two categories:

- Surface impurities: there are minor soluble components (mainly Mg, Ca, K salts, etc.) and insoluble components (clay, sand, loam, etc.) on the surface of the salt crystal structure; this portion may amount to far more than 30 %.
- Inter-crystalline impurities: due to the uncontrolled crystallization process, minor soluble components and also insoluble components are included into the NaCl lattice.

The impurities of the first category can be eliminated with mechanical processes (salt washing, etc.) up to a certain degree. The inter-crystalline impurities, however, can only be eliminated by dissolving and recrystallizing the salt.

The demand of the industry for high-purity and low-priced NaCl is constantly increasing, in particular in Asia. With its energy efficiency and the low emission values (waste products), a modern recrystallization plant can form a cost-effective alternative to other known vacuum salt technologies.

This article describes the principle of recrystallization, presents the present state of the art, compares the process with other principles (multiple effect evaporation, mechanical vapour recompression) for manufacturing vacuum salt, and gives an overview over the recrystallization plants in operation today.

2. HISTORY

In the potash industry, vacuum cooling plants entered the field at the end of World War I already. The plants had 1-2, later 3 evaporators in a vertical design, into which the hot salt solution was introduced laterally at the bottom and sprayed into the evaporation space. Later on, the number of stages was increased to avoid scaling in the evaporators above all, and to better utilize the temperature gradient. The vacuum cooling plant (system Lurgi) for cooling raw potash brines consisted of agitator-type evaporators with several stages, surface condensers and a mixing condenser. The hot solution flowed through the stages of the plant. With an increased vacuum, generated by a water ring pump, vapours were extracted, which in the surface condensers were condensed with the fresh brine pumped through in a counter-flow. The last stages were connected to the mixing condenser. Plants with 15 to 25 stages were built for the crystallization of potassium chloride [1].

In the late 1940's at the Watkins Glen, New York Refinery of the International Salt Company, the first plant model of a sodium chloride recrystallizer was constructed and operated (Richards Process). A 25 tons per day pilot plant was successfully operated for some time [2, 3, 4]. It was as a result of the excellent operation of this second pilot plant that a full scale double-effect unit with 15 tons of salt per hour was constructed and placed on stream at Avery Island, Louisiana, in 1958.

The „Pompe à sel“ process of the Société Industrielle et Commerciale de la Compagnie des Salins du Midi from the year of 1951 is based on the same principle of recrystallization by dissolving the raw rock salt at high temperatures and retrieving the evaporator salt by flash evaporation and simultaneous cooling in a closed circle [5, 6]. Later on, flash evaporation was also used for concentrated, gypseous seawater brine. With German-French technology an installation with a annual capacity of 60,000 to 70,000 metric tons of salt was established in Cabo Frio, Brazil [7].

3. PROCESS DESCRIPTION

The vacuum cooling plants use the principle of adiabatic flash evaporation, which is also well known from the operation of multistage flash (MSF) plants for seawater desalination [8]. A hot solution is gradually relieved to a lower pressure level. Thus part of the water evaporates and the solution is concentrated.

In the case of NaCl recrystallization, the feed solution is hot saturated brine and the stages are special forced recirculation crystallizers without a heating chamber. In the individual crystallizers, the solution is supersaturated due to the evaporation of water and due to the decreasing solubility of NaCl with decreasing pressure and brine temperature, and therefore NaCl crystallizes. The salt suspension is removed from the crystallizer via an elutriation column and subsequently supplied to the salt debrining and drying plant (centrifuge and dryer). In the elutriation column, the salt is classified, cooled and cleaned with the counter-brine (displacement of the mother liquor). The brine (mother liquor) is transferred from one stage to the next and in each crystallizer NaCl is precipitated. One part of the produced salt crystals results from the evaporation of water from the saturated brine and the other part from the cooling of the saturated brine.

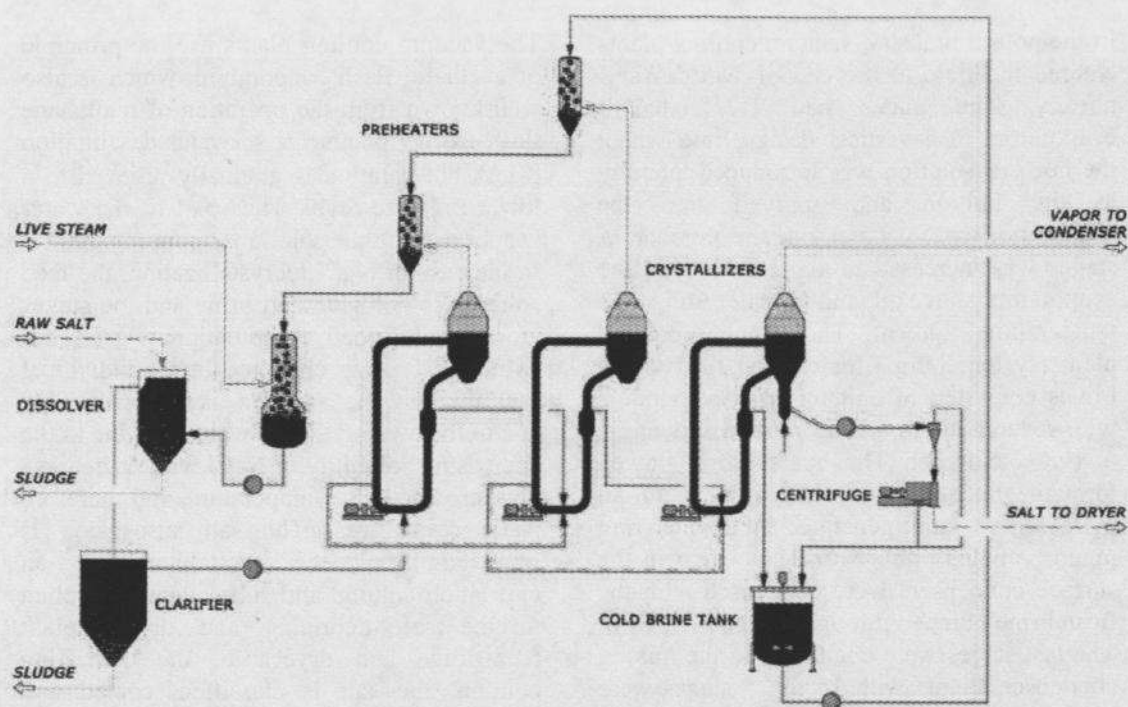


Figure 1. Recrystallization with hot raw salt dissolving (Triple-effect)

The cold purge from the last stage therefore is saturated with NaCl. This brine is transferred into mixing pre-heater columns, where it is heated by the respective vapours and simultaneously also diluted. This is also an adiabatic process. At the first glance, a special phenomenon can be observed in that. The diluted brine exiting the mixing pre-heater is warmer than the exhaust vapours themselves. The system is in thermo-dynamic equilibrium. The system pressure is equal to the pressure of the exhaust vapours and the temperature of the solution corresponds to the saturated vapour temperature of the vapours plus the respective boiling point increase. The brine from the last mixing pre-heater stage is thus undersaturated and according the number of stages between 85°C and 100°C hot. In order to achieve the full saturation capacity and to compensate for the heat losses, the brine is heated to the operating temperature of approx. 108°C in further live steam-heated pre-heaters.

In the salt saturator, the brine is saturated by adding crystalline raw salt. A good portion of the insoluble components and the calcium sulphate are sedimented and removed from the brine. The brine circle is complete and the brine can be transferred into the flash crystallizers (Figure 1).

The vapours from the last stage are condensed on a condenser, whereat due to the lower required dT (logarithmic temperature difference between vapour and cooling water), a mixing condenser is to be preferred over a surface condenser. From a thermo-dynamic point of view, these vapours have to be considered a loss, since they cannot be used further for preheating the cycle brine.

The more flash stages are planned, at same production capacity, the smaller the specific vapour load per stage becomes, and thus the losses from the last stage decreases as well. The number of stages, however, cannot be increased at random. The number of the stages is determined by the total economic efficiency of the project. According to our state of knowledge only one 7-stage installation is in operation worldwide (Bad Friedrichshall, Germany).

For the hot dissolution process, the hot brine temperature is approximately the atmospheric boiling temperature of the saturated brine (108°C). The cold brine temperature is determined by the vapour pressure of the last stage. This again is determined by the available cooling water temperature [9, 10, 11].

3.1 Heat and mass balance considerations

As mentioned at the beginning, on the brine-side, the recrystallization process is an (almost) closed cycle. Losses in the water balance mainly occur due to the vapours of the last stage, the sludge drain and the residual moisture of the recrystallized salt. The vapours of the last stage, which cannot be used for pre-heating anymore either, form the main sink for the heat losses. Beside the radiation losses, heat is likewise removed from the process with the salt and the sludge. Depending on the relation between heat and water loss, these may be returned into the process with a live steam-heated mixing and/or surface pre-heater.

3.2 Hot or cold dissolution?

This question is discussed controversially again and again. Universal rules for the selection of the adequate dissolution process are difficult to set up. In the following, the most important advantages and disadvantages of the individual processes are to be highlighted:

Hot dissolution process

As is known, CaSO_4 shows inverse solubility, i.e. with increasing temperature, the solubility decreases rapidly (Figure 2). The hot dissolution process therefore has the big advantage that the raw salt (rock or solar salt) with CaSO_4 impurities is dissolved at that point of the process, where the residual solubility of the CaSO_4 is lowest. The residual contents of dissolved CaSO_4 in the hot brine is that low that in the further flash process no more CaSO_4 is precipitated, even if the entire available range is utilized. The maximum concentration of sulphate in the brine circuit is between 1500 and 3600 mg per liter. A

higher calcium concentration lowers the sulphate concentration according the solubility product. The reasons for non-stoichiometric calcium concentrations are CaCl_2 impurities in the raw salt feed and alkalisation of the brine circuit with milk of lime. Alkalisation with caustic soda precipitates, with absorbed CO_2 from the atmosphere, a small calcium carbonate amount. On the whole the CaSO_4 separation takes place without the addition of chemicals. A further substantial advantage of this process also lies in the possibility to remove large amounts of insoluble matter from the saturated brine, before they get into the flash crystallizers or pre-heaters. The sedimentation process in the dissolver benefits from the temperature-related low viscosity of the hot brine. By adding flocculants, a good portion of the undissolved foreign substances taken along from the dissolver can be removed in downstream decanters and sand filters. Thus, the susceptibility to scaling of the crystallizers is clearly reduced, which again has a positive effect on the availability of the plant. Respectively designed hot dissolution processes can manage raw salt qualities with a portion of foreign substances of 30 and more weight percent without any problem. Such low raw salt qualities are quite frequent. They may, for example, originate from sea salt plants or from salt mining.

On the other hand, the process is demanding in regards to apparatuses and procedures. Beside the abrasion characteristics of the undissolved solids, the low pH value, the high temperature and the degree of oxygen saturation of the brine have to be particularly considered in materials selection. The solid-liquid separation (brine decantation, brine filtration) downstream of the dissolver also work at over 100°C , which is not entirely unproblematic either.

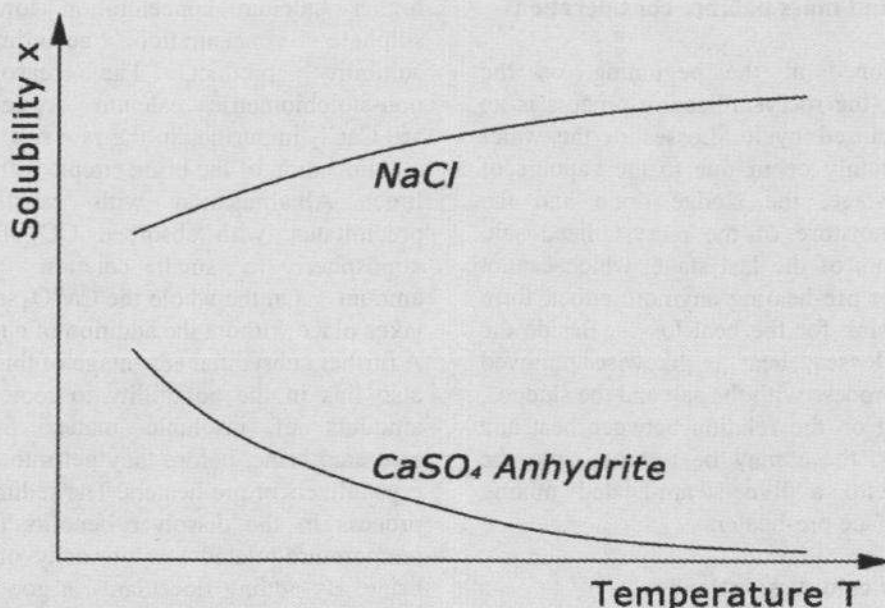


Figure 2. Solubility trend of CaSO_4 Anhydrite in saturated brine

Cold dissolution process

As the expression implies already, the raw materials supply in the process part takes place at the lowest temperature, i.e. after the last flash stage. The cold brine, which leaves the last stage, is saturated with NaCl . Thus the raw salt is not dissolved, but only a salt suspension is mashed. This is then pumped through the mixing pre-heaters, in which it is partially dissolved due to heating and dilution with the vapours. After the last pre-heater stage, a hot, undersaturated brine has likewise formed. The insoluble portions, however, remain in the brine, and similar to the hot dissolution process, have to be removed from the brine mechanically (decantation, filtration). The final saturation of the brine must still be carried out in a saturator.

As mentioned above already, the solubility of CaSO_4 is inverse. With increasing temperature in the individual mixing pre-heater columns, the dissolved CaSO_4 portion in the brine should actually increase to the solubility limit. Because of the very slow dissolution process and the slow reduction of the supersaturation only a part of the CaSO_4 crystals dragged along is dissolved. But finally also this small portion of dissolved CaSO_4 is crystallized in the flash crystallizers and can cause incrustation.

The advantages of this process surely lie in the technical area. The materials selection is less critical and the equipment tend to become smaller. Without the hot dissolver, the heat losses are smaller, too. The sulphate

portion in the brine is higher than with the hot dissolution process, which has a negative effect on the salt purity. The portion of insoluble matter is passed through the pre-heater columns before it is separated. The undissolved components can form deposits and scaling in the pre-heaters, which reduces the plant availability.

In summary, it can be said that the cold dissolution process can be used in cases, where the raw salt quality is relatively good, i.e. with low contents of insoluble matter, and the cold brine temperature is not too low (e.g. recrystallization with vapour compression).

3.3. Brine treatment

One of the big advantages of this process results due to the circumstance that the sulphate removal can take place either entirely without chemicals or only with the addition of a very small amount of chemicals. The raw salt, however, depending to its origin, still has a number of other components, which have to be removed from the brine.

Insoluble impurities

These are loam, clay, sand, carbonates, silicates, etc. Due to their hardness, they may cause abrasion damage to apparatuses and machines and they give the salt a greyish / brownish colour. These impurities are also not soluble in the hot brine and can only be separated from the brine mechanically. These insoluble substances are normally present in

smallest particle sizes and can only be decanted off using sedimentation agents (flocclulants). A complete separation is procedurally difficult and can only take place in two steps, e.g. by sedimentation and filtration. The insolubles are removed from the process for further drainage and disposal in the form of sludge. In certain use cases, cleaning of only a partial flow, e.g. counter-flow brine to the elutriation column, may be sufficient, too.

An efficient sludge drainage is of high significance. The higher the remaining residual brine quantity in the sludge, the higher are the brine losses from the circuit.

Soluble impurities

Beside CaSO_4 , still further soluble salts, like e.g. magnesium and potassium compounds, can be found in the raw salt. The magnesium content has to be observed. In case of higher magnesium concentrations in the starting product, an additional magnesium precipitation by adding CaO may be necessary. Normally, however, an alkalisation of the hot brine to about pH 8-10 is sufficient, which for corrosion reduction, too, is very desirable. Some residual ions like potassium, bromide, nitrate, etc. are not precipitated and must be purged from the process in their liquid form. In most cases, the mother liquor

quantity of the sludge is sufficient for liquid purge.

3.4 Recrystallization with mechanical vapour recompression

The combination of recrystallization with mechanical vapour recompression (MVR) represents an interesting variant of this process (Figure 3). The vapour cycle is completed by compressing the vapours from the last stage using compressors that much that they may be reused as heating steam. Thus, the process becomes almost adiabatic. The maximum compression ratio "Beta" of modern centrifugal compressors is a little above than 2. With two compressors connected in series, a saturated vapour temperature increase of about 45-50°K may thus be achieved. The use of more than two compressors is economically not reasonable anymore and represents an additional procedural problem. Thus, the operating pressure of the last stage is determined as well, which is substantially higher than for the recrystallization concept with live steam heating. Due to the smaller temperature spread, recrystallization plants with MVR must be operated with considerably higher brine volumes as in live steam heating plants with the same production capacity.

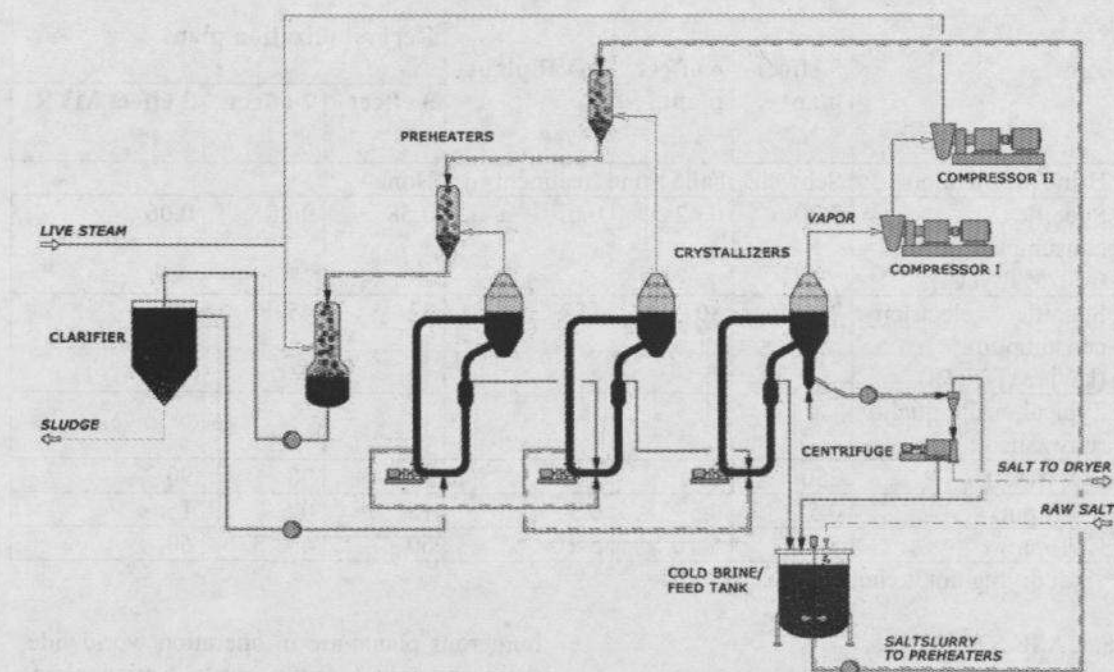


Figure 3. Recrystallization with cold raw salt dissolving (Triple-effect and MVR)

The steam and cooling water consumption for this process is almost zero. The heat losses are for the most part compensated by the isentropic enthalpy increase of the vapours by the compressors. Depending on the water and heat balance, the use of an additional mixing or surface pre-heater might be required as well.

4. COMPARISON OF PROCESSES AND LIMITATIONS OF USE [12, 13]

The table 1 gives comparison values in regards to the specific energy consumptions of the individual vacuum salt processes.

Advantages of the recrystallization procedure are the abolition of the classical chemical brine purification and the possibility of the use of raw salts with high calcium sulphate contents. The procedure has a almost neutral water balance, therefore it can be used also in water-poor regions. All three vacuum salt procedures supply a salt quality with a sodium chloride content from at least 99.95 %, at what the recrystallization salt is characterized through a low sulphate content of approx. 100 ppm (max.) and the salts from the multiple effect and MVR processes by the

low calcium content of less than 10 ppm.

Normally the energy consumption for salt recrystallization is lower than for multiple effect or MVR plants. But the energy consumption of recrystallizers depends from the raw salt quality and the residual hot brine content of the insolubles which leave the dissolvers and debrining equipment for disposal. For example, worse raw salt with 30 % insolubles increases the specific steam consumption to 720-750 kg per metric ton of vacuum salt.

The specific investment costs are not stated, since they are very similar, i.e. maximum deviation of +/- 20 %, and they should not be relevant for decision-making.

Contrary to the multi-stage and MVR processes, the maximum capacity of recrystallization plants is rather small. With multiple effect installations and with MVR installations, capacities of 100-150 MT of NaCl per hour can be achieved without any problem; for recrystallization, the economical limit is about 20-40 MT NaCl per hour. The main reason for this is that for this process, very large amounts of brine have to be recirculated and therefore the apparatuses and machines can have very large dimensions.

Table 1. Process comparison

Process	5 effect plant	6 effect plant	MVR plant	Recrystallization plant		
				3 effect	7 effect	3 effect MVR
Brine purification	Schweizerhalle brine treatment			None		
Specific steam consumption* (MT/MT NaCl)	0.70	0.62	0.01	0.58	0.45	0.06
Specific electricity consumption* (kWh/MT NaCl)	25	30	155	32	45	80
Typical salt quality (unwashed):						
SO ₄ (ppm)	250	250	250	90	90	90
Mg (ppm)	0.5	0.5	0.5	15	0.5	15
Ca (ppm)	5-10	5-10	5-10	60	40	60

* Salt drying not included.

5. CASE STUDIES

Compared to salt works, which work according to the multi-stage or the thermo-compression principle, of which

numerous plants are in operation worldwide, there are only a few recrystallization plants (see Table 2). In the following, some of the plants for recrystallization of rock salt and solar salt in operation today are described in

more detail.

5.1 Borth, Germany

The first plant in Germany based on the Pompe-à-sel process was built by Escher-Wyss at Solvay in Borth in 1962/63. The 3-stage plant uses thermo-compression and was equipped with a multi-stage centrifugal compressor. In the plant, fine-grained rock salt from the Borth rock salt mine is processed. The supply of the salt works with rock salt takes place either

directly from the Borth pit or during the mining-free period from storage. The salt works are for the most part built as an open-air plant; only the sensitive machines and equipment are accommodated in buildings. In the evaporator area, only little high-quality steel is used. In order to manage corrosion, sacrificial anodes are installed. The original output of the plant amounted to about 600 metric tons of evaporated salt per day with a brine cycle of 800-1000 m³/h [10].

Table 2. Recrystallizers for sodium chloride

Location	Borth, Germany	El Outaya, Algeria	Bad Friedrichs-hall, Germany	Cankiri, Turkey	Semnan, Iran	Chittagong, Bangladesh
Operating company	Esco	Enasel	Südsalz	Med-Mar	Sabzdasht	Confidence Salt
Start-up	1963	1983	1995	2002	2003	2005
Raw salt origin	Rock salt	Rock salt	Rock salt	Rock salt	Rock salt	Sea salt
Raw salt Quality (NaCl, grain size)	98-99%, 0-2 mm	97 %	85 %, 1-12 mm, or 98.5 %, 0.16-2 mm		90-92%	65-75%
Dissolving process	cold	cold	hot	hot	hot	hot
Number of effects	3	3	7	3	3	3
Operating temperature range	120-75°C (1 st effect with over-pressure)	100-65°C	102-45°C		90-50°C	90-50°C
Brine circuit (m ³ /h)	1500		450		70	160
Heating	MVR ¹⁾	MVR ²⁾	Live steam (2 bar abs., with cogen ³⁾)		Live steam	Live steam (with cogen ⁴⁾)
Cooling water (m ³ /h)	-	-	360-450 (circuit)		180	340
Nominal capacity (MT NaCl/hour)	30	18	20	10	5	10
Annual salt production (1000 MT)	260	30	160-190		35	60

1) 7-stage radial compressor (1963); 2 compressors serial (today)

2) 1-stage radial compressors, 2 parallel and 1 serial

3) cogeneration by gas and steam turbines

4) cogeneration by a diesel engine

5.2 Bad Friedrichshall, Germany

After the Staatliche Saline Friedrichshall had dealt with tests and studies for re-crystallization of rock salt since 1954 already, the successor company Südwestdeutsche Salz AG in Bad Friedrichshall-Kochendorf/Germany

commissioned a 7-stage recrystallization plant for rock salt in 1969. Responsible for the engineering was the company Bureau Technique pour l'Industrie Chimique Kaltenbach, Paris. This refinery processed ferrocyanide-free Muschelkalk rock salt from the Kochendorf mine, the salt content of which lay between 95 and 98 %. The plant

was dimensioned for an annual production of 60,000 metric tons of evaporated salt, later on an annual amount of 80,000 metric tons could be generated with optimisations. The flash evaporators were designed in rubber-lined steel and set up barometrically (see Figure 4).

The steam supply took place from a heavy oil-fired cogeneration plant. This evaporated salt plant was the replacement for several open pan salt works in the south-west German area, which were shut down.

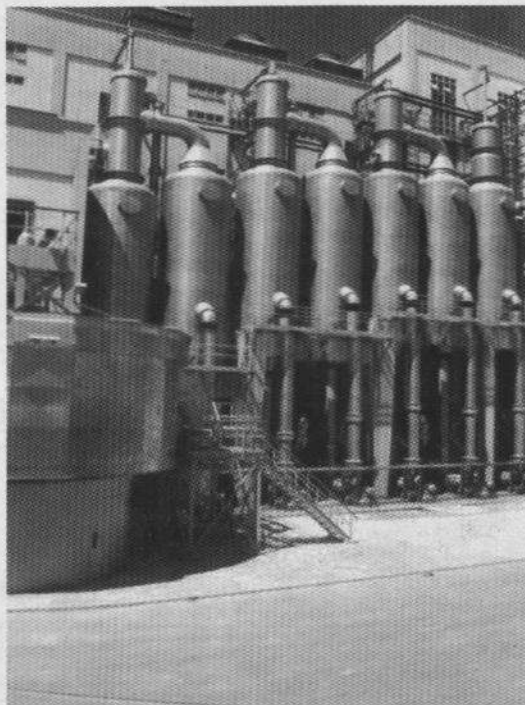


Fig. 4. Barometric installation of flash evaporators at the Bad Friedrichshall salt factory (1969-1995)

In 1995, a bigger flash evaporation plant replaced the plant from 1969, whereat HPD-Evatherm acted as the engineering partner. The new plant has an output of 20 MT/h and processes rock salt from the Heilbronn salt mine. The saturation of the weak brine from the evaporator cycle takes place in the bottom-up process in vertical dissolution apparatuses, in which the undissolved natural impurities (clay, anhydrite) of the rock salt are left behind. In order to remove the dissolution residues, the process is switched over to another dissolver, so that a quasi-continuous dissolution process is guaranteed. Before the entrance into the saturator, the weak brine returning from the pre-heater columns with 100 °C is heated up to the boiling point (approx. 108 °C) with low-pressure steam from a gas-fired cogeneration plant. The separation of fine undissolved particles entrained from the saturators takes place in a heat-insulated

decanter with a downstream sand filter. Before the entrance into the first evaporator, low heat losses of the saturated brine are compensated by indirect heating with steam. The seven evaporator bodies are manufactured from different materials: Monel, rubber-lined steel, Avesta. In order to avoid corrosion in the evaporation plant, the brine is slightly alkalised with sodium hydroxide solution (pH 9-10); this also results in the magnesium and amphoteric aluminium traces contained in the raw salt either remaining undissolved or being precipitated as hydroxide. The use of sacrificial anodes is not required. The dissolution residues are brought to the Kochendorf mine for backfilling cavities. Independent of which raw salt quality is processed in the plant, the result is an evaporated salt with invariable high purity, which is suited for all applications, even for the pharmaceutical area (see Table 3).

Table 3. Qualities of rock salt feed examples and vacuum salt in the Bad Friedrichshall salt factory

	Rock salt (Type 1)	Rock salt (Type 2)	Vacuum salt (dried)
Grain size	1-12 mm	0.16-2 mm (max. 7 % below 0.16 mm)	0-1 mm (d' 0.4 mm, < 0.16 mm max. 5 %)
NaCl (dry substance)	85 %	98.5 %	99.98 %
Moisture (120°C, 2 hrs)	4 %	0.1 %	0.05 %
Calcium	1.2 %	0.12 %	40 ppm
Magnesium	30-50 ppm	30-50 ppm	0.5 ppm
Potassium	50-100 ppm	50-100 ppm	20 ppm
Bromide	30-40 ppm	30-40 ppm	15 ppm
Sulphate	3 %	0.28 %	90 ppm
Insolubles	12 %	1.1 %	< 10 ppm

For that, washing the salt on the pusher-type centrifuges is not required. A worse raw salt quality, however, increases the specific energy consumption and reduces the annual

vacuum salt output of the plant. However, processing non-marketable rock salt qualities supports the economic operation of the Heilbronn salt mine.



Fig. 5. New 7-effect recrystallization plant at Bad Friedrichshall, under erection

5.3 Yingkou, China

Beside the annual production capacity of

800,000 metric tons of sea salt, the Yingkou Salt Industry Corp. Ltd, situated in the southern part of Liaoning Province, have introduced a flash evaporation sea salt recrystallization. The plant is designed as

triple-effect recrystallizer with an annual production capacity of 150,000 metric tons of vacuum salt [14]. The estimated energy consumptions are 750 kg steam and 42 kWh per metric ton of salt.

5.4 El Outaya, Algeria

In Northern Africa (El Outaya, Algeria), a recrystallization plant for rock salt was erected as a consequence of an Algerian-American joint venture technology transfer case in 1983. The rock salt processed here is extracted in open pit mining from a nearby diapir. The plant is dimensioned for a salt production of 22 MT/h and is equipped with a combination of two parallel single-stage compressors, connected in series with a third unit [10].

The evaporated salt produced has a purity of at least 99.75 %, with contents of max. 100 ppm of calcium, max. 10 ppm of magnesium, and max. 500 ppm of insolubles. The El Outaya salt refinery near Biskra is located no more than 20 miles from the most visually impressive of the Saharan oases.

5.5 Chittagong, Bangladesh

The salt works commissioned in 2005 is the first vacuum salt plant of this type on the Indian subcontinent. As raw material, solar salt with a salt content of no more than 65-70 % is available. The solar salt cannot be properly upgraded with a salt washing plant; therefore the recrystallization plant represents a logical process choice. The plant is a three-stage recrystallization plant using hot dissolution; the capacity per hour amounts to 10 MT/h.

The specialty of this plant is the high portion of insoluble substances, which has to be separated from the hot brine. The sludge from the dissolvers is pumped into big sedimentation basins. In order to minimise the losses from the purge, the clear brine from the sedimentation basin is returned into the cycle. From an energetic point of view, the plant in Chittagong is an autarkic operation. A Diesel aggregate generates the required electrical energy, whereat the waste heat (hot water) is used to pre-heat the cycle brine.

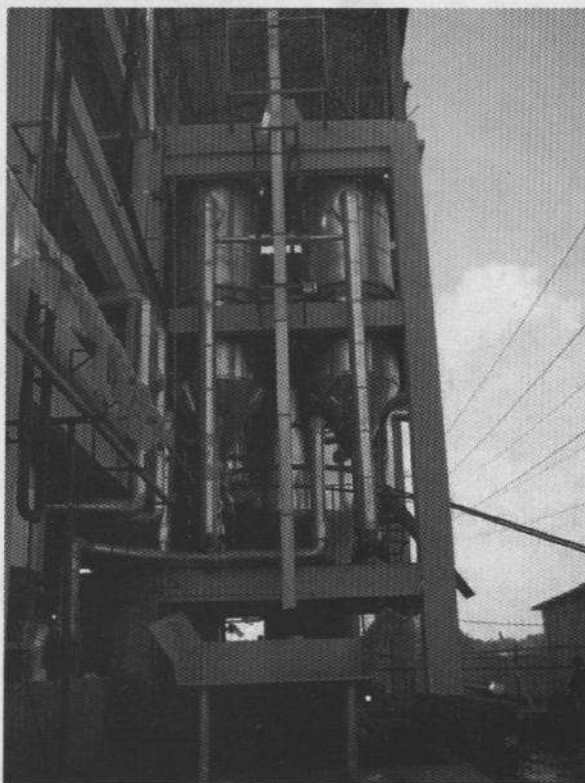


Fig. 6: Saturators of the Chittagong plant, Bangladesh

Keywords: Recrystallization, upgrading, rock salt, solar salt

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