

Physical and Chemical Phenomena Accompanying Thermal Evaporation of Raw Brine

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ABSTRACT

Numerous processes are used or are suggested to reduce the difficulties encountered by thermal evaporation of raw brine with all its original impurities. Here one considers the experimental conditions of this evaporation using germination, without purification prior to feeding the evaporators. The influence of the various related parameters are then studied as well as interdependent incidences of conditions involved in the implementation of an industrial process.

Results reported are based on experience of an industrial producer of refined salt, interested in seawater desalting problems.

SUMMARY OF TREATMENTS USED PRIOR TO EVAPORATION

The raw material available for production of salt by thermal evaporation is generally a raw brine obtained by dissolving halite from injected water or from non-controlled underground water. This raw brine, saturated with sodium chloride, also contains impurities such as Na, Ca, Mg, SO_4 , the hypothetical groups of which can be: CaSO_4 , MgSO_4 , Na_2SO_4 , CaCl_2 , MgCl_2 .

As far as calcium sulphate is concerned, the raw brine is generally saturated. Heating and evaporation of such a brine leads to precipitation of sulphate onto the heating surfaces and, depending on temperature and concentration factors, to a partial hydrolysis of the Mg ion which can cause accidents because of corrosion.

Apart from partial or total purification of raw brine by precipitation of alkaline earth and sulphate ions (the process the most used industrially), sundry other preliminary treatments have been proposed to limit introduction of calcium sulphate into solution or to increase its solubility over and above concentration obtained when dissolving sodium chloride. The six treatments are as follows.

1. Sequestration of calcium and magnesium by sodium hexametaphosphate¹. The sequestration agent avoids crystallization of alkaline earth salts. The quantity of sodium hexametaphosphate required is eight times the

quantity of calcium sulphate existing in the brine, 45 g/l for example, for a 5.5 g/l CaSO_4 content.

2. Addition to solution water injected into the saliferous deposit of an alkaline carbonate and an alkaline phosphate soluble in water² in a $\frac{\text{Na}_2\text{O}}{\text{P}_2\text{O}_5}$ ratio defined by the quantity of calcium contained in the raw brine.
3. Dissolving of halite with water "vaccinated" by means of an alkaline polyphosphate³.
4. Addition to the dissolution water of a small quantity of an alkaline carbonate and alkaline polyphosphate⁴, or addition to dissolving water of an alkaline polyphosphate and of a heavy metal ion, in particular aluminum⁵.
5. Use of water having a minimum pH of 7 and containing sodium carbonate and tribasic sodium phosphate⁶. Addition to the brine of an alkaline phosphate treated with starch and recirculation of mother brine⁷.
6. Addition to a raw brine, upstream from the evaporators, of a small quantity of sodium hexametaphosphate (5–100 ppm)⁸. Solubility of calcium sulphate is thus doubled. This avoids scaling by limiting the concentration factor to 2 and temperatures to 100°C. This allows a pure salt to be produced; 50 to 60% of the feed brine are then bled. The brine thus bled is recirculated to the head of the plant into the evaporators operating at a higher temperature, with germination.

These processes only give a brine having a calcium sulphate content lower than saturation. They involve a few problems. There is high reagent consumption of polyphosphate and sodium carbonate. The processes are unusable or have no effect upon the brines obtained from water of underground origin, except for process (6). The brine pH must be adjusted (process 5). These processes limit the concentration factor of brine but do not solve the problem of elimination of impurities. They require the use of bleeds according to another process, otherwise the discharge would be too high. Mother brine is bled, concentrated in soluble calcium sulphate, and must then be evaporated by means of a sulphate germination process. Handling this mother brine bleed by conventional purification processes (see below) would be just as costly as applying these to raw brine.

BRINE EVAPORATION WITH PRIOR PURIFICATION—SALT PRODUCED

In plants where refined salt is produced, either a pure saturated brine, a purified saturated brine or even a raw brine are evaporated. Let us consider here the first two cases with a view to their later comparison with raw brine evaporation.

Evaporation of a completely purified saturated brine.

Most often this brine is prepared by dissolving a salt having a low rate of impurities (for example, raw sea salt having 99.7% NaCl dry content). Prior to feeding the evaporation plant, this brine is submitted to a calcosodic treatment (lime or caustic soda and soda ash) to eliminate the alkaline earth ions. This is followed by a treatment with a barium salt (highly expensive) to precipitate the SO_4 ion. This brine gives rise to crystallization of a fine salt whose typical characteristics are as follows:

Internal moisture	400 to 600 ppm
(Weight loss at 550°C of a sample submitted to a prior drying at 110°C down to constant weight.)	
SO_4	50 ppm
Ca	< 3 ppm
Mg	< 1 ppm
Heavy metals (as metal oxides)	< 10 ppm
NaCl (as dry)	99.99 %

Evaporation of a brine submitted to prior purification, with recirculation. The brine is ridden of alkaline earth salts and heavy metals by alkalization and carbonatation (recirculation of mother brines, lime and CO_2 treatment and possibly with sodium carbonate). Conditions for purification of this brine require a recirculation flow of the bleeds amounting to about 50% of the output which is to be evaporated. Thus there is a concentration rate of SO_4 ions into the feed brine much greater than that of the original raw brine.

Chemical characteristics of the fine salt produced, after light claircing, can be the following:

Internal moisture	1.200 to 2000 ppm
SO_4	500 to 600 ppm
Ca	< 3 ppm
Mg	< 1 ppm
Heavy metals	< 10 ppm
NaCl (as dry)	99.94 to 99.95%

Sulfate content can be lowered by large claircing but this will dissolve an undesirable quantity of salt. It is difficult to lower this sulphate content below 80–100 ppm.

Evaporation of previously purified brine by a mere calco-sodic treatment. Because of anti-pollution requirements relating to the environment, this process cannot be considered without bleed recovery (10 to 20% of the feed flow) and treatment of the latter, for instance in a soda works. The salt produced has the purity level given in the above, except that of sulphate, which depends on the SO_4 content of purified brine liable to be used for washing and clarifying purposes. 150 to 200 ppm SO_4 are generally obtained with the salt.

RAW BRINE EVAPORATION WITH GERMINATION

“Raw” brine. Typical chemical compositions are shown in Table 1. The solubility of calcium sulphate in saturated brine without other impurities is 4.6 g/kg water at 20°C. This solubility is 3.7 g/kg water at 110°C and 2.9 g/kg water at 130°C⁹. For raw brine, type 1 or 2, the variation of solubility of calcium sulphate in terms of temperature rise remains practically the same.

In a temperature range of 20–70°C, without prior seeding, these brines will precipitate, by heating and evaporation, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), between 70–85°C $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (hemihydrate) and, beyond, CaSO_4 (anhydrite).

TABLE 1
Chemical Composition of “Raw” Brine.
Brine Composition g/l—15°C.

Salts	Type 1 ¹ (SO_4 ion excess with respect to alkaline earths)	Type 2 ² (reverse excess)
NaCl	309.0	309.0
CaSO_4	4.08	5.3
MgSO_4	2.2	0.5
MgCl_2	—	2.0
Na_2SO_4	7.0	—
CaCl_2	—	—

¹Brine frequently obtained from non-controlled underground water.

²Brine frequently obtained from surface water injected.

Evaporation plant. Before analyzing the phenomena accompanying evaporation of raw brine, we briefly describe the industrial plant we operate and how it works. This plant has a yield of 600,000 tons/year fine salt (= "vacuum" salt). It consists of a first, single unit operated by recompression while a second unit operates in 5 stages (Fig. 1). In France, we do not call it "vacuum" as in the English-speaking countries because neither "vacuum" nor "pressure" are characteristic factors for salt crystallization, and in this specific case, our yield is attained to the extent of two thirds under pressure superior to the atmospheric pressure.

The entire plant is fed with raw brine, except for the 5th stage which is fed with brine purified by a calco-sodic treatment. Temperatures of the mother brine in boiling conditions are as follows:

Thermo-compression	116°C
1st stage	124°C
2nd stage	105°C
3rd stage	86°C
4th stage	69°C
5th stage	49°C

Raw brine used here is produced by injection of river water into the halite deposit. It is type 2.

Internal treatment in evaporators. In each of the evaporators fed with raw brine, some lime milk is injected into the mother brine. This injection which supplies OH^- ions is regulated. A practical means consists in using an industrial pH-meter. Its reading should be maintained between 8 and 9.

The magnesium ion fed by the raw brine is precipitated as magnesium hydroxide and the possible high temperature hydrolysis if this ion is avoided (no corrosion accident). Calcium is eliminated by heating and evaporation as crystallized sulphate except for Ca which remains partly as a soluble CaCl_2 , since this is a type 2 brine. The CaCl_2 will be eliminated with the sludge part of the bleed.

Conditions of germination. Considering the chemical composition of the mother brine which is controlled "in situ" and, for the 4th stage, the seeding cited below, calcium sulphate precipitates as anhydrite. This remains in suspension as does magnesium hydroxide. Anhydrite concentration of the suspension is maintained between 25 g and 30 g/liter by bleed regulation. In the coolest elements it can increase advantageously to 40 or even 50 g/l. Crystalline suspension thus consists of anhydrite at about 80% and magnesium hydroxide at about 20%. Because the raw brine is saturated with calcium sulphate, and has a low alkaline earth chloride content, it is readily possible to reach a concentration factor of 5 without it being necessary to recirculate the germs.

Bleeds are re-injected from the hottest evaporator towards the coldest to maintain and develop anhydrite crystal-

line seeding in the whole plant. This is done to avoid formation of hemihydrate in the 3rd stage bodies and to reduce gypsum formation almost totally in the 4th stage bodies. The final bleed is settled. The clear overflow is recirculated while the underflow is eliminated.

Salt produced. Average chemical characteristics of fine salt produced are:

Internal moisture	500 to 700 ppm
SO_4	120 to 150 ppm
Ca	45 to 70 ppm
Mg	< 1 ppm
Heavy metals (as metal oxides)	< 10 ppm
NaCl (as dry)	99.97 to 99.98%

SUNDRY CONDITIONS AND FORMS OF PRECIPITATIONS

It has been seen that in this plant, where the raw brine is type 2, sulphate is precipitated as anhydrite. Type 1 brines have also been tested with and without internal alkalinizing treatment.

Precipitations for brine type 1. If the conditions of evaporation (temperature less than 70°C) did not entail a corrosion risk and accordingly if they did not require alkalization in evaporation, then the magnesium concentration rate in the mother brine would increase. Where the concentration factor is greater than 10 or 12, for a high magnesium content in the raw brine (as 1 g/l for example), magnesium crystallizes as double sulphate which might be löweite $3[\text{Na}_{12} \text{Mg}_7 (\text{SO}_4)_{13-15} \text{H}_2\text{O}]$, or van't hoffite $[\text{Na}_6 \text{Mg} (\text{SO}_4)_4]$. Crystalline suspension would then consist of calcium sulphate and a double magnesium/sodium sulphate. This would avoid consuming an alkalinizing agent whilst obtaining a salt of a commercial grade (NaCl # 99.9%).

If, with this same type 1 brine, OH^- ions are introduced by treating the mother brine with lime or with caustic soda, a syn-crystallization of calcium sulphate and sodium sulphate is obtained in this Na^+ saturated medium, in one of the following forms^{10, 11}.

Over 110°C	= $\text{Na}_2\text{SO}_4, \text{CaSO}_4$
Over 90°C	= $\text{Na}_2\text{SO}_{4.5} \text{CaSO}_{4.5} \text{H}_2\text{O}$
Over 70°C	= $2\text{Na}_2\text{SO}_4, \text{CaSO}_{4.2} \text{H}_2\text{O}$

Precipitations for brine type 2. If the conditions of evaporation allow for concentration without fear of corrosion, we could increase magnesium concentration rate up to very high levels. Where the concentration factor is 10 to 12, greater than the values quoted for germination (factor = 5), we have ascertained that at temperatures above 85°C, there is hydrolysis of the Mg ion and a suspension consisting of anhydrite and magnesium hydroxide. The precipitation of complex chloride or sulphate has not been observed.

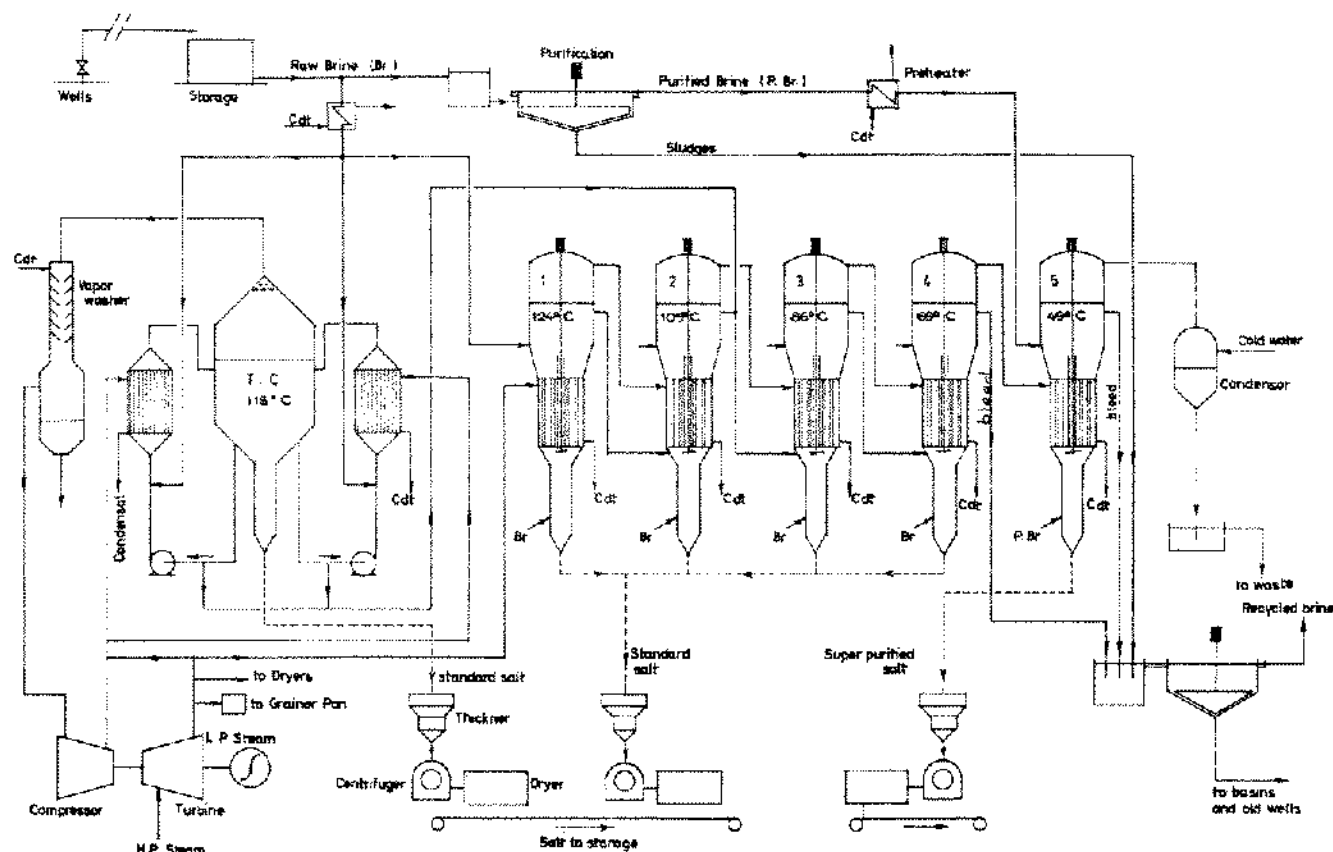


Figure 1. Diagram of plant operated for refined salt production.

But if for this same type 2 brine the mother brine is treated by lime (as in the above described plant), it can be seen that anhydrite is precipitated. If we substitute caustic soda for lime we again obtain the same results as before, i.e. double sodium and calcium sulphate.

It has been seen that the best operating conditions for the equipment and the most efficient elutriation are recorded when sulphate precipitation occurs as anhydrite CaSO_4 . It is thus advisable to carry out a treatment in the mother brine which leads to anhydrite crystallization. The principle of this "in situ" treatment¹² is basically differentiated from a preliminary purification of the raw brine before its feeding because the reactions occur under quite different conditions of concentration and temperature: i.e. those of mother brine. This process is at the origin of an important improvement of the salt produced at industrial scale by "high suspension".

The evaporating plant whose characteristics were described has operated since 1966 without any scaling of heating surfaces. However, we wish to mention an incident which occurred during this period. For some time, the anhydrite suspension dropped accidentally to approximately 10 g/l in the first two stages. A temperature and yield drop was then recorded and this corresponded to a scaling of the heating surfaces. Complete elimination of the calcium sul-

phate scale was obtained by increasing the anhydrite suspension for 48 hours and maintaining at 40–50 g/l (by bleed reduction). Temperatures and output then returned to their regular level. We checked during a maintenance check of the evaporators that tube surfaces were free from all scaling. No other chemical or mechanical de-scaling process was able to give such a perfect result. During studies we made relating to seawater concentration, we noted the same de-scaling phenomenon again.

Case of marine brines. It was interesting to check whether conditions of germination, applied to seawater concentration in a concentration factor range less than 5, gave rise to the same results as those recorded with salt production.

From 1968 to 1973, our studies with the "Commissariat à l'Energie Atomique" (Grenoble Centre for Nuclear Studies) were the subject of various papers^{13, 14, 15}. Seawater has a lower calcium sulphate content than that of saturated brine, i.e. 1.3 g/liter for standard seawater¹⁶. Precipitation takes place as anhydrite.

Because water is being concentrated in an open loop system, it is essential to separate and reinject a given quantity of crystalline germs at the head of the preheating system in order to maintain suspension of anhydrite at the required value. Therefore, whilst maintaining the anhydrite suspen-

sion at a value ranging between 25 and 35 g/liter between the inlet of the preheating system and the flash evaporation, we experimentally checked the lack of calcium sulphate, calcium carbonate and magnesium hydroxide deposits.

PURITIES AND IMPURITIES OF SALT PRODUCED

Table 2 shows the different analyses of the salts produced. In the germination process, mother brine in evaporators contains a crystallized salt. In the germination process the grain size of the solid impurities is much smaller than the salt. When extracted a good quality sodium chloride must not contain grains less than 180 μ . The calcium sulphate is 6–25 μ , the magnesium hydroxide is 4–6 μ . A double backflow washing with limpid brine (raw brine) in the leg of the evaporator and in a thickener-washer unit provides an almost total separation of the solid impurities.

The hydraulic transfer of the salt from the evaporator to the thickener cooperates to this separation. Practically all the particles tending to adhere to crystal surfaces are loosened during this transfer. We thus feed the centrifuger with a slurry made of limpid brine and crystallized salt. The impurities of salt produced are practically reduced to those occluded to or included in the crystals and those dissolved into the brine film coating each crystal salt. We can thus affirm the interest in carrying out germination with an anhydrite suspension rather than with that of hemihydrate or gypsum. The crystals of the latter are much larger than those of anhydrite. The proper salt/calcium sulphate separation allows for limitation of impurities in salt produced to a quantity very close to that of the included calcium sulphate.

The comparative table shows of course that the purest salt is the one obtained from a desulphated pure brine. It can be noted in particular that occluded water and sulphate content are very low.

Salt obtained from crystallization of a raw brine in presence of a calcium sulphate germination with an in situ treatment of the mother brine has sulphate and occluded

water content much lower than those of salt obtained by crystallization of a previously purified brine (not desulphated). This is due to the low SO_4 ion content in the mother brine. At 110°C for example, solubility of calcium sulphate expressed as SO_4 is approximately 0.7 g/l in a brine saturated with NaCl. It is even lower in a mother brine issued from a type 2 brine, and treated in situ with lime, because of CaCl_2 concentration which has taken place. This again is an advantage of the treatment.

It has been noticed that the low SO_4 concentration rate gives rise to a low occlusion content¹⁷ of about 600 ppm in the germination process and even less in the case of use of pure brine (desulphated).

In the earlier discussion we saw that prior treatments of brine other than conventional purification processes (in particular those with polyphosphate) avoid scaling and give a fairly pure salt. This is provided that the bleed flow is such that calcium sulphate solubility is not reached⁸. Such a treatment provides a salt of fair purity in the coldest pans and permits to transfer germination to the hottest pans where sulphate will be eliminated as anhydrite. However, the occluded water content of the salt produced in the low temperature pans is still much greater than that of a high suspension salt.

BLEEDING—RECOVERY OF BRINE LOSSES

Through evaporation of raw brine, impurities which are insolubilized, calcium sulphate (anhydrite) and magnesium hydroxide are driven along by the bleed flow and separated by decanting while the clear effluent is recirculated. Residues obtained as a thick sludge can be stored in existing underground cavities and this allows the recovery of an equal quantity of raw brine by transfer. On the whole, a quantity of brine equal to that of the bleed is recovered.

With regard to impurities which remain soluble (for example, CaCl_2 , formed by the action of lime on MgCl_2), recirculating the clear effluent gives rise to a higher CaCl_2

TABLE 2
Brine Treatment Process and Characteristics of the Produced Product

Characteristics of the Produced Salt	Brine Treatment Process		
	Prior Calco-Sodic and Barium Salt Purification	Prior Calco-Sodic Purification With Recirculation	Germination With "In Situ" Treatment (As Required)
Occluded water ¹	400–600 ppm	1200–2000 ppm	500–700 ppm
SO_4	#50 ppm	500–600 ppm ²	120–150 ppm ³
Ca	< 3 ppm	< 3 ppm	45–70 ppm
Mg	< 1 ppm	< 1 ppm	< 1 ppm
Heavy metals (as metal oxides)	<10 ppm	<10 ppm	<10 ppm
NaCl, as dry, %	99.99%	99.94–99.95%	99.97–99.98%

¹For a same grain size distribution (200–500 μ).

²With a slight clarifying.

³Without clarifying.

rate in the evaporators but, at last, CaCl_2 is eliminated with the liquid fraction of the sludge. Where on the one hand, the conventional purification processes of raw brine (upstream from the evaporation plant) handles the entire quantity of raw brine and recirculated bleed flow, on the other hand with germination the separation of impurities is made only on the bleed flow. This is less than 15% of the feed flow, and means that facilities have a smaller capacity.

Besides the considerable saving of reagents the germination process reduces considerably the equipment required for the separation of impurities brought by the raw brine.

CONCLUSIONS

With all types of currently available brine including seawater, sulphate germination ensures a scaling-free heating and evaporation process.

As far as salt production is concerned, the development of this process, the control of mother brine composition, as well as of crystallization which occurs in, it enabled us to make considerable progress towards an adequate purity of the product. We now currently reach 99.98% instead of 99.85% which was the purity level of "high suspension" salts manufactured two decades ago. The sulphate content is very low. Magnesium is quite eliminated. It is only if all trace of calcium were to be removed, that this salt would be unsuitable.

This process gives a salt with a low aqueous occlusion content. In particular this salt is perfectly suited for the electrolysis of the molten NaCl for the manufacture of metal sodium. Furthermore, one can note that anhydrite is insoluble in the molten salt and, therefore, there are no SO_4 ions liable to damage the electrodes (traces of calcium chloride do not matter in this case). Costly purification with a barium salt can thus be avoided.

No appreciable influence of the process on grain size distribution of the salt has been noticed. The elutriation it involves is an adequate factor for the reduction of "fines", which is always advisable.

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