A New Process for the Washing of Solar Salt

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ABSTRACT

In order to meet the purity requirements of its more and more demanding industrial market, the COMPAGNIE des SALINS du MIDI et des SALINES de DJIBOUTI and its subsidiary companies have been developing for a few years a new process for the washing of solar salt. The process makes it possible to ship high purity sodium chloride without preliminary storage period. The product can be used by electrochemical industries equipped with mercury cathode cells, known to be particularly sensitive to impurities, without costly treatments for purification.

Two techniques, whose application to high capacity handling of solar salt can be considered as fairly original, are the main features of the process: hydraulic transport of salt-brine mixtures and continuous centrifuging.

The facility described in these pages has an hourly capacity of 750 metric tons, which is planned to be increased to one thousand. It is located in France, at AIGUES-MORTES, by the Mediterranean sea.

I. GENERAL DESCRIPTION OF THE PLANT

Handling and Dumping of Harvested Salt

Handling of harvested salt from the crystallizers is secured by sets of two tilting trailers pulled by agriculture type tractors. Salt is dumped into large steel plate hoppers fitted in concrete pits. The top of the hopper and the pit, at same level as the ground, is covered with a grate made of parallel rails allowing traffic of the vehicles. This arrangement, usual in solar salt industry, secures quick dumping of salt without the maneuver of trailers.

The bottom of the hopper is fitted with a control gate, circular sector shaped, operated from outside through a segment-gear and driving wheel device, so as to adjust the flow of salt towards the mixing chamber.

Mixing of Salt with Washing Brine

When passing the gate, salt falls into a mixing chamber receiving the flow of washing brine delivered from the settling ponds by centrifugal pump, controlled through an ordinary type gate-valve.

The mixture salt brine, with checked proportions, is fed to the suction entry of the mixture pump, located slightly below the mixing chamber, opposite to the brine inlet. This pump, of special design and construction, can handle salt-brine mixtures with proportions required by hydraulic transport into pipes, that is around 40 tons of salt for 100 cu. m. of mixture (20% in volume of salt in the mixture).

Figure 1. Washing plant of Aigues-Mortes – General View.

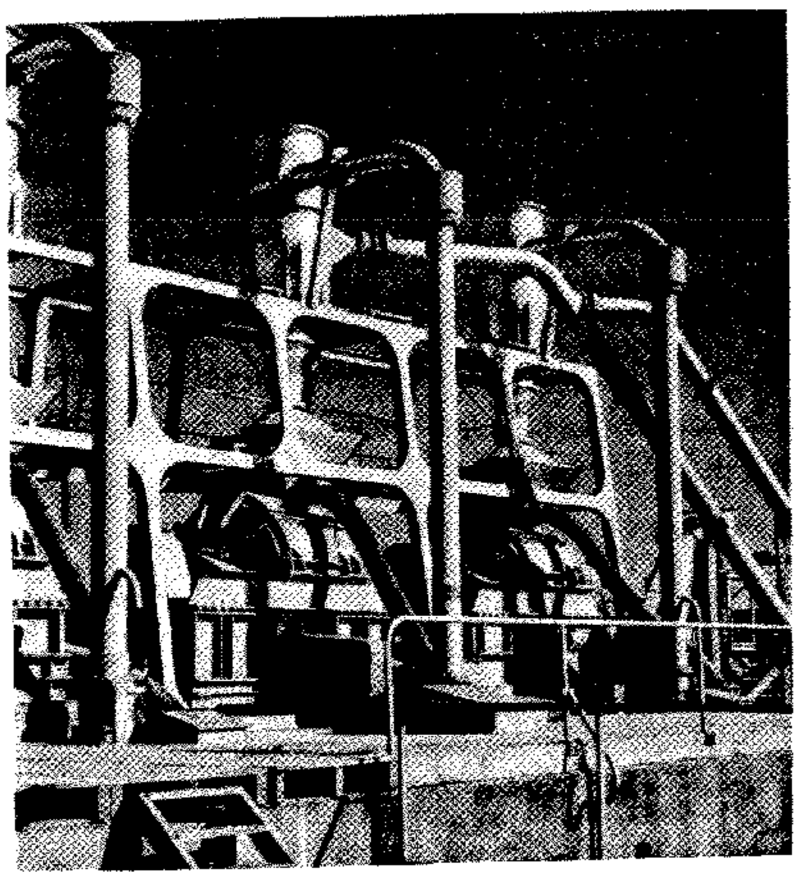


Figure 2. Washing plant of Aigues-Mortes – Hydrocyclones and Centrifuges.

The pressures, flow speeds and types of pipes have required some research work for correct adjustment; hydraulic transport of crude salt is now widely used in the plants of the Company and can be considered as fairly well investigated.

Thickening of Salt-Brine Mixture

The mixture delivered by the pump into PVC or steel pipes has to be thickened before centrifuging. This is done either by hydrocyclones or by grate-drainers, or else by combinations of the two types of thickeners, as it is the case at AIGUES-MORTES.

The mixture is delivered first under some 1 kg./sq.cm. of pressure to ordinary steel plate hydrocyclones. Some adjustments of the cyclones make it possible to discharge through the overflow most of the washing brine together with the finest insoluble matter. At the underflow, the slurry out of the cyclones consists of the salt and some of the washing brine. It falls over a conical grate-drainer which completes the washing out of insoluble matter and secures the feeding of the centrifuges with steady brine content.

Centrifuging

The mixture out of the second thickener is fed to high capacity centrifuges. These machines have been designed and developed after long experiments both in the factory and on the saltworks during the harvest time. The hourly capacity could be brought up to 250 metric tons of product. The centrifuges are of the horizontal axis vibrating type. They are equipped with 1.3 m. diameter stainless steel bowls made of trapezoidal cross section welded bars with 0.4 mm. wide slots.

Thanks to the vibrating equipment, which spares any blade or pusher discharger on one hand, to the low speed of rotation (300 r.p.m.) on the other hand, breakage of crystals is kept to a very low rate.

The centrifuging equipment is constructed by the German firm SIEBTECHNIK, MULHEIM (Rhur).

At AIGUES-MORTES, three hydrocyclone-grate drainer-centrifuge sets are located on the same framework above the storage belt conveyor. The salt-brine mixture is delivered either from two hoppers close by the washing plant or from a long distance hydraulic transport. The washing, centrifuging and storage operations can thus be centralized from several dumping places corresponding to the main groups of crystallizers.

Settling and Control of Washing Brines

The overflows of the hydrocyclones are collected in a concrete pit together with the filtrates out of the thickeners and centrifuges from where they are delivered by pumping to the settling ponds.

Arrangement and dike work of these ponds allow settling of solid matter gathered by the brine during washing as well as continuous discharge and renewal of the brines circuit; the inlet can consist either of freshly saturated brine from the condensers or of low concentration water.

By adjusting discharge and renewal it is possible to keep constant the chemical properties of washing brines at the required level, decided in advance according to the quality of washing to be achieved. The chemical composition of brines are checked on site at regular intervals by quick tests developed by the Control Laboratory.

II. CHEMICAL PURIFICATION IN THE NEW WASHING PROCESS

As far as chemical washing of solar salt is concerned, and particularly elimination of calcium and magnesium, the new process proved to give results which were generally considered out of reach of the former methods.

Calcium

From initial ion calcium contents of around 0.10 to 0.15%, the former washing plant of AIGUES-MORTES could deliver salt containing, at the best, 0.07%. From same calcium impurities entering the plant, the present washing commonly achieves final contents below 0.04%. This can be considered as a somewhat unexpected advantage of the pump hydrocyclone-centrifuge system. The reason could be that part of the calcium sulphate consists of very fine crystals (below 0.1 mm.), that separate out in the overflow of the hydrocyclones. As a general rule, it was constantly observed that the final calcium contents are half of the usual figures obtained in older types washing plants.

Magnesium

Washing out of magnesium is a constant concern for salt producers supplying electrochemical industries.

The following example will help to visualize the phenomena involved in this particular purification of salt and to figure out the quantities at stake.

Supposing that the requirement of the customer, at the time of delivery is: Mg content $\leqslant$ 0.025% (expressed in ion magnesium percentage), how should washing be operated and what would be the losses rate? Comparison will be made between the two processes:

1. Washing and draining
2. Washing and centrifuging

Most of the magnesium remaining in salt after storage is due to the soluble magnesium salts contained in the brines accompanying washed salt to the stockpile.

In fact, solar salt is usually dispatched after several months of storage. During the storage period, natural dripping of the stockpile and rain water action improve to an appreciable extent the chemical washing achieved at the time of harvesting. This depends on the amount and date of rainfalls during the winter (or storage).

The requirement of 0.025% Mg at the time of delivery corresponds then to higher contents in washed salt. From the average observations at AIGUES-MORTES, this could be figured out as follows:

1. Washing and draining:

September:	stockpiled salt	(12% moisture) (0.08% Mg content)
May:	dispatched salt	(3 to 4% moisture) (0.025% Mg content)

2. Washing and centrifuging:

September:	stockpiled salt	(3.5% moisture) (0.06% Mg content)
May:	dispatched salt	(3 to 4% moisture) (0.025% Mg content)

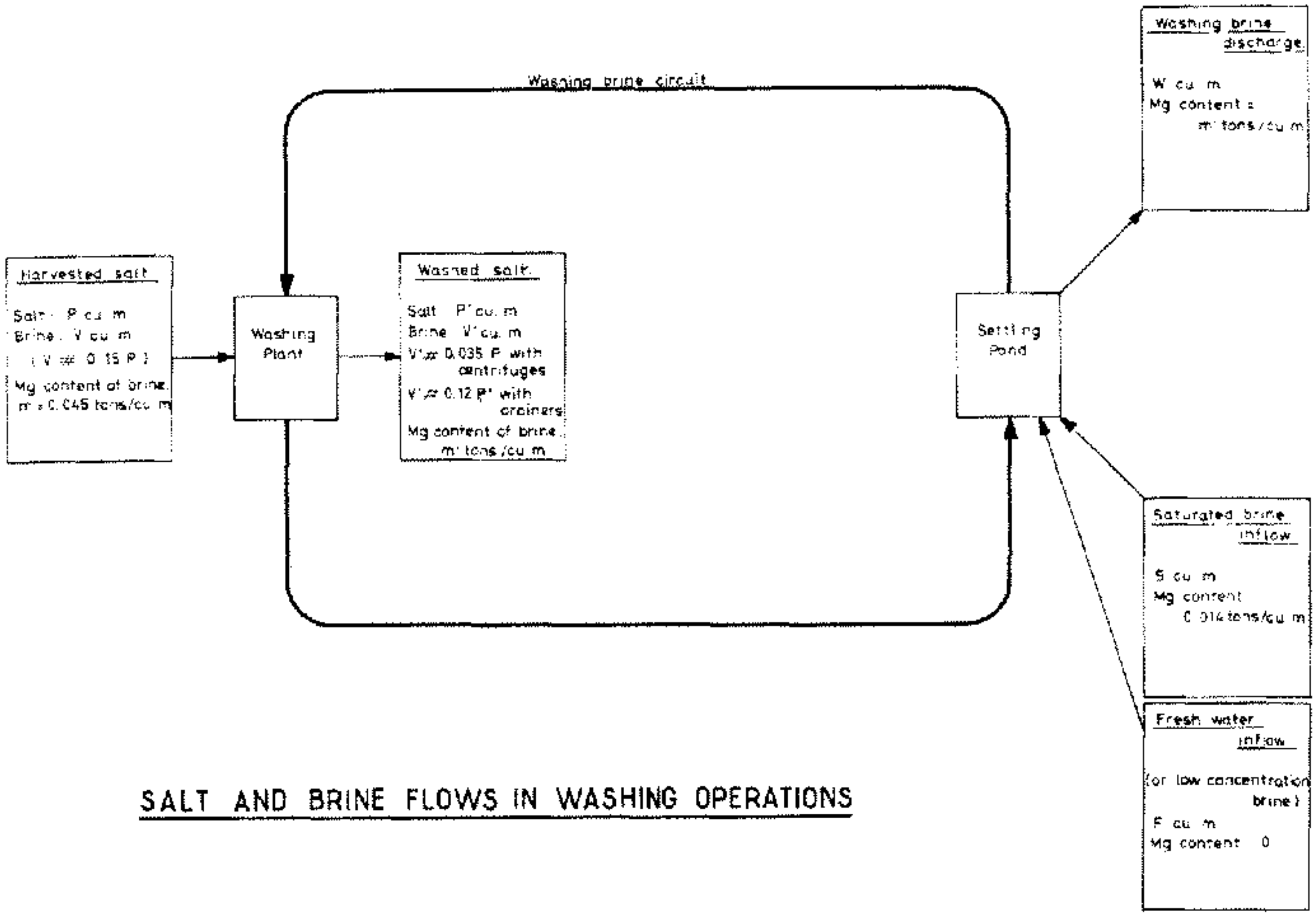
The difference between the two series of figures is due to the fact that with the former process the moisture of stockpiled salt was much higher and natural dripping of the stock more important; for the same final requirement, the Mg content of washed salt could have been a little higher.

The maximum Mg contents after washing being then defined in both cases, it is possible to figure out the flows of products through the plant, as shown on the enclosed diagram; in fact, to make this approximate example clearer, the balance of the circuit will be reduced to two relations only, concerning the volumes of different brines in and out the plant on the one hand, and the quantities of magnesium (ion) on the other hand.

1. Washing and draining:

After washing and draining to 12% moisture, the Mg content of salt should not exceed 0.08%. The maximum Mg content in washing brine is then:

$$m' = \frac{0.08}{100 \times 0.12} \# \frac{0.007 \text{ tons/cu. m.}}{\text{(or 7 g/liter)}}$$



SALT AND BRINE FLOWS IN WASHING OPERATIONS

The Mg content of freshly saturated brine from the condensers being around 0.014 tons/cu. m. it appears that such purity requirement can only be achieved by means of fresh water inflow in the brine circuit.

The balance of the circuit can be written down as follows:

Brine: $0.15\,P + F = 0.12\,P' + W$

Mg : $0.15\,P \times 0.045 = (0.12\,P' + W)\ 0.007$

For P = 1 cu. m. (≠ 1 ton) we find: F = 0.8 cu. m. of fresh water

This implies losses by dissolution amounting roughly to 0.320 tons per cu. meter of fresh water entering the circuit[1] (solubility of NaCl). In this case, these losses would be then $0.8 \times 0.320 = 0.25$ tons, that is to say 25% of washed salt.

2. Washing and centrifuging:

The requirement for centrifuged salt at 3.5% moisture being 0.06% Mg maximum, we find:

maximum Mg content in washing brine:

$$\frac{0.06}{100 \times 0.035} = \begin{array}{c} 0.017 \text{ tons/cu. m.} \\ (17 \text{ g/liter}) \end{array}$$

[1] In fact, part of the salt dissolved is fine salt (filtrates) which would have been lost in any case. The losses by dissolution are actually below the computed values of this example.

It could be possible in this case to use, for renewal of the brine circuit, freshly saturated brine, containing 14 g/liter of Mg.

To compare the two washing processes, it will be assumed, as previously stated, that the renewal consists only of fresh water.

Balance of brine circuit:

Brine: $0.15\,P + F = 0.035\,P' + W$

Mg : $0.15\,P \times 0.045 = (0.035\,P' + W)\,0.017$

For $P = 1$ cu. m. (# 1 ton): $F. = 0.25$ cu. m.

Losses by dissolution: $0.25 \times 0.320 = 0.08$ tons, representing 8% of washed salt.

Instead of supposing, as above, that the final chemical purity achieved by both methods is the same, the computations can start from the hypothesis that the losses by dissolution rate should not exceed a certain maximum; in this case, the final purities in both types of washing will be compared:

Hypothesis: Losses by dissolution should be kept below 15% of washed salt:

For $P = 1$ ton, and with above quotations, it comes:

$$F \times 0.320 \leqslant 0.15$$

Maximum value of $F = 0.47$ cu. m.

The balance can be then written in both cases:

1. Washing and draining:

   Brine: $0.15 + 0.47 = (0.12\,P' + W)$

   Mg : $0.15 \times 0.045 = (0.12\,P' + W) \times m'$,

   m' being the maximum Mg content of washing brine (tons/cu. m.)

   Then: $m' = 0.013$

2. Washing and centrifuging:

   The change of $(0.12\,P' + W)$ by $(0.035\,P' + W)$ obviously does not affect m' which is also found: 0.013 tons/cu. m.

This corresponds, in washed and stockpiled salt, to the following Mg contents:

1. Washing and draining:

   $$0.12 \times 0.013 = 0.155\%$$

   Which, after several months of storage, will give salt containing around 0.05% of Mg.

2. Washing and centrifuging:

   $$0.035 \times 0.013 = 0.045\%$$

   which will give, after storage, a final content of some 0.015% of Mg.

These rough computations show that high purity salt can be obtained by centrifuging with a reasonable amount of losses (which could even be reduced by using freshly saturated brine as circuit renewal), whereas the cost of such purification appears rather high with the conventional washing process.

As far as losses by entrainment are concerned, the advantage of the cyclone and centrifuge system is also valuable: there are practically no salt crystals in the overflow of the hydrocyclones. In the filtrates of the grate-drainers and centrifuges, the losses are about 5% of the salt. This loss rate is far below the one usually observed with conventional buckets or push-plates drainers.

The results can be summarized as follows:

	Washing & Draining		Washing & Centrifuging	
Final Mg content after storage (%)	0.025	0.05	0.015	0.025
Losses by dissolution (%)	25	15	15	8

Double Centrifuging

As mentioned previously, most of the chemical impurities are carried into the brine left in the crystallizer and "harvested" with the salt. This amount of brine is about 10 to 15% of the weight of harvested salt; it is introduced in the washing plant at the same time as the salt.

If a centrifuging operation is carried out before the entry of crude salt to the washing plant itself, only 20% to 30% of the high magnesium and calcium content mother liquor are fed to the plant.

It is then easy to improve the chemical purity of salt up to the most exacting requirements without prohibitive losses.

Crushing of Salt into Brine

In several saltworks harvesting particularly well grained, strong crystals, a crushing stage is successfully introduced in the series of operations above described, yet improving the chemical purity of the salt. The crushers in use, called "MCC," specially designed and set up by the Company, are fitted with a vertical axis rotating blade. The "MCC" are generally located between the thickners, hydrocyclones or grate-drainers, and the centrifuges.

The washing process which has just been described has been working for several years in the rough conditions of the harvest of solar salt in FRANCE, TUNISIA, ETHIOPIA, and MADAGASCAR.

In all the saltworks of the SALINS du MIDI group, the new equipment has replaced washing plants which were considered as up-to-date less than ten years ago.

With smaller capacities, the same process is used by the Company for the treatment of solar salt before drying and packing. The salt thus obtained is perfectly clean and can almost vie with vacuum or other types of evaporated salt.