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Vacuum Salt Plant or Mechanical Refinery? Guidelines for the Selection of the Optimal Process

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Vacuum Salt Plant or Mechanical Refinery? Guidelines for the Selection of the Optimal Process

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ABSTRACT

The greatest part of today's world salt consumption of 200 Mt/year is used directly from natural resources without special purification steps. The estimated production of all vacuum salt plants and salt washing plants (mechanical refineries) is only about 50 Mt per year. Most industrial processes, however, require chemical treatment of intermediate salt solutions to prevent enrichment of impurities if unrefined salt is processed. The more emphasis is given to environmental protection, the more purification of salt prior to the industrial processes becomes necessary. The use of unpurified salt in electrolysis plants, for example, creates environmental problems resulting from the deposit of the precipitation sludges and, moreover, requires expensive chemicals for the brine treatment. Whether mandatory or advisable, salt refinery in turn asks for optimal concepts with regard to technique and economy.

If the salt is dissolved in a brine from nature or from solution mining, there is, of course, no other possibility for salt purification than crystallization. Starting with solid salt from rock salt deposits or from solar ponds, however, requires the decision for either the mechanical or thermal refinery ("salt washing plants" and "recrystallization plant", respectively)

The most important factors influencing this decision are: type and content of the impurities in the crude salt, structure of the raw salt inclusions, required purity of the refined salt as well as total solid-state behaviour (e.g., crystal size distribution, crystal habit, free flowing properties), energy situation on site. Regarding the chemical and physical composition of the crude salt and the desired result it is usual to undertake special laboratory and semi-technical investigations to define the most effective and economical technology for any special case. From hundreds of such investigations a theoretical way could be determined for the preselection of the optimum plant conception with regard to the chemical composition of the purified salt without costly labwork.

INTRODUCTION

The largest part of today's world salt consumption of about 200 Mt/year is directly used as exploited from natural resources without special purification steps (Ullmann, 1979; Winnacker-Küchler, 1982; Römpf, 1991). With approx. 65%, the chemical industry is the main salt user (Fig. 1). The estimated production of all vacuum salt plants and salt washing plants (mechanical refineries) is about 50 Mt/year.

Most industrial processes, however, require chemical treatment of intermediate salt solutions to prevent the inclusion of impurities, if unrefined salt is processed. The more emphasis is laid on environmental protection, the more purification of salt prior to the industrial processes becomes necessary. The use of unpurified salt in electrolysis plants, for example, creates environmental problems resulting from the depositing of precipitation sludges and, moreover, requires expensive chemicals for the brine treatment.

Whether mandatory or advisable, salt refinery in turn asks for optimal concepts with regard to technique and economy. If salt in a solid state is required and if this crude salt is dissolved in a brine from nature or from solution mining, crystallization will be the main purification step. Starting with solid salt from rock salt deposits or from solar ponds, however, requires the decision for either the mechanical or thermal refinery ("salt washing plant" and "recrystallization plant", respectively).

RAW SALTS

There are two different types of crude salt: salts from solar ponds, i.e. products that are recovered by solar evaporation, and rock salts. The main impurities found in rock salt are anhydrite (CaSO_4) and water-insoluble mineral constituents. Rock salt contains only minor proportions of soluble impurities.

Salt from solar ponds contains both insoluble and

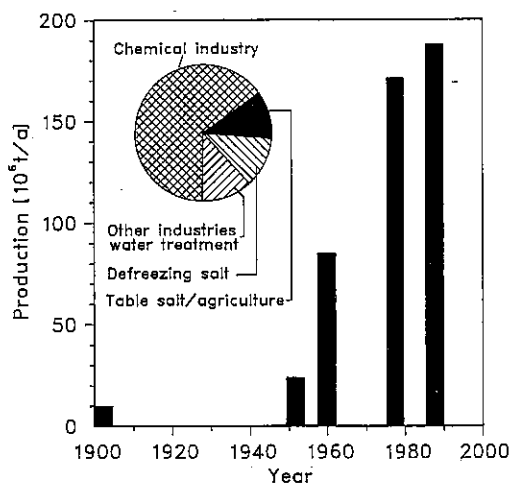


Fig. 1. Salt production and use of salt world wide.

soluble impurities. Experience with salts originating from 30 countries — from South America to the Far East — was collected and the results prepared in the form of distribution diagrams (Figs. 2–4). Particular emphasis was laid on the analyses of NaCl, KCl, $MgCl_2$, $MgSO_4$, $CaSO_4$, water insolubles, drying losses and particle-size distributions. From these analyses it is possible to derive a typical composition of salt from solar ponds and to see the limits for the range of variations. The variation of impurities mainly results from local conditions such as the control of the solar evaporation process and the subsequent salt harvest. The theoretical mass balance of a seawater solar evaporation process, as shown in Fig. 5, demonstrates that with an optimum mode of operation the calcium sulphate precipitates as gypsum before sodium chloride crystallization. If the gypsum and salt crystallization processes are effected in separate ponds — subject to the degree of evaporation — the salt crystallization will yield a product with a $CaSO_4$ content of 0.65–0.76%. The soluble impurities in the solar salt originate from the adherent mother liquor and constituents that are included in the crystal.

The precipitation of soluble salts starting with the astrakanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) will be effected in the solar pond only if the brine is further concentrated beyond the concentration of 32°Be indicated in Fig. 5. Table 1 gives a summary of the statistical key values of the analyses of about 100 different crude salts. The average value contains the arithmetical mean, the most frequent value represents the maximum of frequency distribution and the range of variations comprises the proportion of sum distribution with frequencies between 16 and 84%. These data may be taken as a basis to determine a probable and a typical salt composition. Also

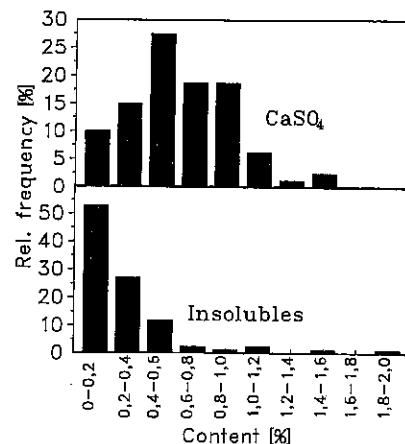


Fig. 2. Frequency distribution of insoluble impurities in crude sea salt.

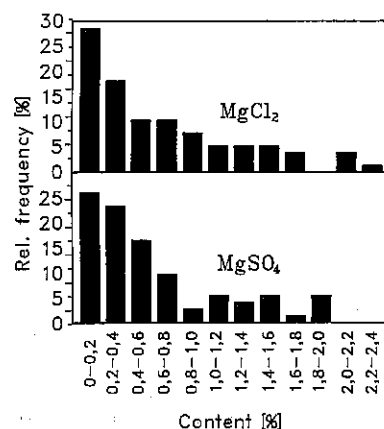


Fig. 3. Frequency distribution of Mg compounds in crude sea salt.

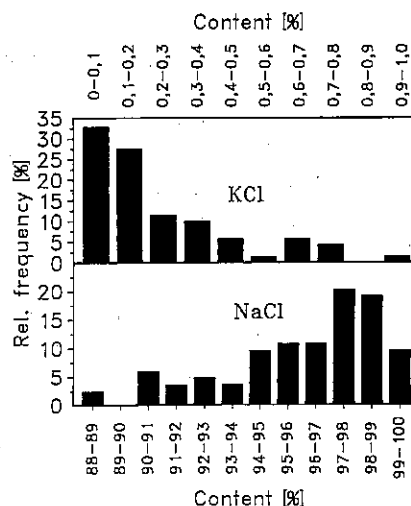


Fig. 4. Frequency distribution of KCl and NaCl in crude sea salt.

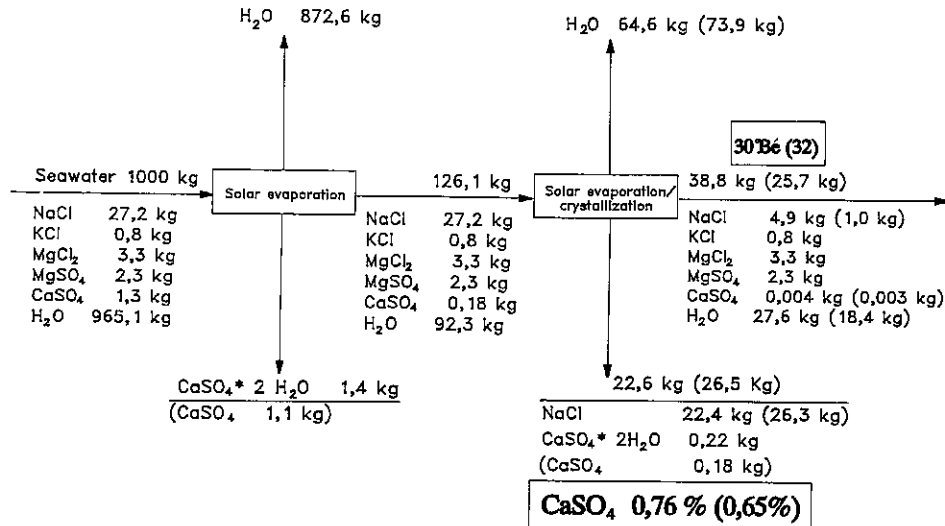


Fig. 5. Solar evaporation of seawater.

TABLE 1
Typical characteristics of sea salt from solar ponds

	Average	Most frequent value class	Zone of dispersion
NaCl %	96.10	97-98	92.4-99.7
KCl %	0.24	0-0.1	0.03-0.44
MgCl ₂ %	0.66	0-0.2	0-1.28
MgSO ₄ %	0.59	0-0.2	0.16-1.05
CaSO ₄ %	0.62	0.4-0.6	0.28-0.92
Insolubles %	0.29	0-0.2	0.08-0.44
Dry loss %	4.36	1-2	1.8-7.9
RRSB plot:			
Mean size mm	3.75	2-3	1.9-5.9
Uniformity	1.80	1.75-2	1.4-2.1

the form of frequency distributions is explicable. For CaSO₄ and NaCl a frequency maximum under the equilibrium conditions in the evaporation process is as expected, whereas for the soluble matters the frequency distributions do not show a maximum but a constant drop (of a log standard distribution type) owing to the more or less perfect liquid/solid separation in the solar pond.

HYDROMECHANICAL SALT WASHING

Figure 6 shows the functioning of a hydromechanical salt washing plant. The crude salt, which optionally may have been ground before, is fed into a washing vessel equipped with a built-in overflow facility. The up-flow velocity in this zone is regulated to such an extent that only fine particles can be withdrawn. The salt slurry is conveyed by a pump into a hydrocyclone for pre-concentration and from there into a washing thickener. Both in the hydrocyclone and in the washing thickener, fine particles are withdrawn and returned to the washing vessel.

A continuously operating centrifuge is used to separate the salt slurry from the liquid and to wash the salt. This is the only point where water is introduced into the process. Figure 7 shows the effect of the purity improvement by displacement of the adherent solution on the centrifuge.

The overflow from the washing vessel is conveyed to a settling pond, where the undissolved fine particles, i.e. fine NaCl, CaSO₄, 2H₂O and water insolubles are taken out as a purge from the lower section. The entrained liquid must be replaced by fresh water. The solids-free overflow of this settling pond is used as washing liquid in the washing thick-

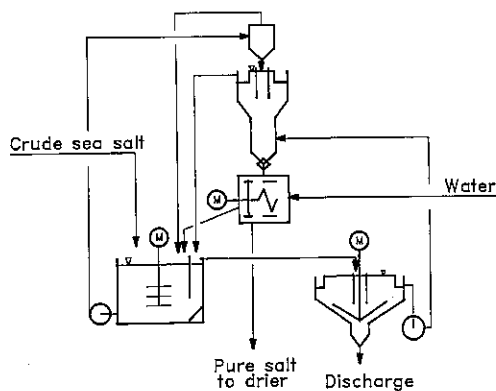


Fig. 6. Salt washing plant.

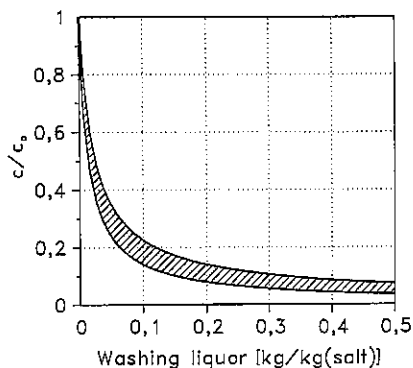


Fig. 7. Effect of impurity displacement on centrifuge by washing. c/c_0 , Rel. impurity factor.

ener. The higher the content of undissolved particles on the crude salt and the lower their compressibility, the larger is the quantity of water that is discharged along with the solids. Accordingly more fresh water must be fed into the process. With this fed-in water quantity the content of impurities in the circulation quantity and the salt yield are determined.

If the content of undissolved substances is low and if the slurry purge has a high solids content, for a salt with a high content of soluble impurities an additional solution discharge may be required to obtain a high salt purity.

OBTAINABLE NaCl QUALITIES IN THE HYDROMECHANICAL SALT WASHING PROCESS

With the purpose of elaborating the most generally applicable rule possible for the determination of obtainable salt qualities as a function of the respective crude salt, a large number of analyses made on crude salt and the washed product were brought into correlation. Figures 8 and 9 show these correlations for soluble and insoluble impurities.

For the soluble-impurities salts a reduction down to a tenth of the initial values has taken place. Calcium sulphate and water-insoluble substances, on the other hand, show quite different conditions. A separation from the salt is only possible if these substances are present *beside* the crystals, i.e. if they are not included in the salt and if the mean sedimentation velocities are different. Figure 10 shows the behaviour of two different crude salts at variable up-flow velocities. A considerable purification is possible, if the particle-size distribution is adapted. The renewed rise of the gypsum content in salt 2 with increasing up-flow velocity is caused by the unfavourable particle-size distribution of the substances to be separated:

Proportionally more NaCl than CaSO_4 is withdrawn at a higher velocity. As an upper boundary line for the insolubles, Fig. 9 reveals practically no separation and thus no purification effect. This phenomenon is observed in very few salts only, which may then be upgraded by a well-aimed size reduction process to such an extent that a successful purification becomes possible.

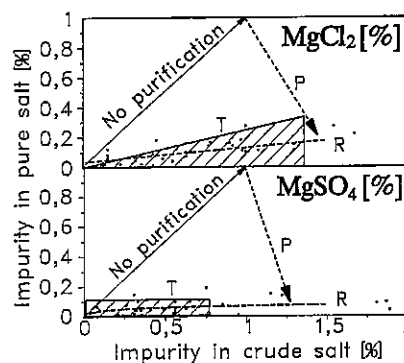


Fig. 8. Correlation between crude salt and pure salt (magnesium compounds). P, Effect of purification; R, regression line; T, typical range.

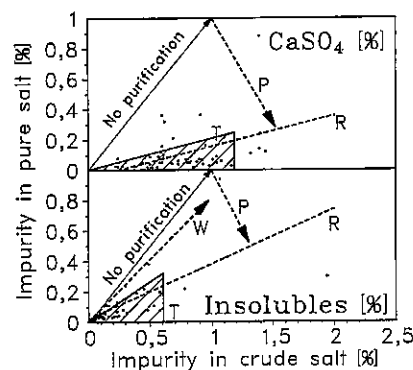


Fig. 9. Correlation between crude salt and pure salt (calcium sulphate and insolubles). P, Effect of purification; R, regression line; T, typical range; W, washing without size reduction.

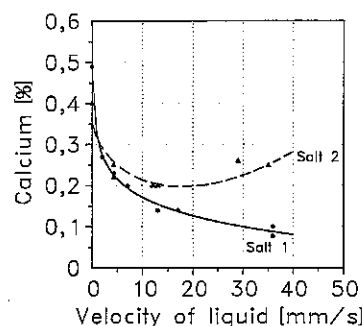


Fig. 10. Purification of salt by washing. Separation of gypsum.

On condition that the solar ponds are properly operated and the washing plants optimally designed, it is possible — as was shown — to obtain an NaCl content of > 98.5%, in most cases even > 99%. The soluble impurities can be reduced to 0.3% (calculated as compounds), the CaSO₄ content to 0.3%. Often, the colour of a salt plays an important role in the successful sale of table salt because in the judgement of salt its purity and its degree of whiteness are unconsciously connected with each other. Generally, the colour can only be slightly influenced by a hydromechanical washing process.

The quality of rock salt cannot be improved considerably in washing plants because in this type of salt there are generally only very little concentrations of soluble impurities and the anhydrite — owing to its mineral structure — will extensively defy a separate degradation. Other than in solar salt CaSO₄ in rock salt is homogeneously distributed, it is included in the salt crystals. However, in special cases, e.g. if the crude salt contains higher amounts of insoluble matter, having a different hydro-mechanical behaviour than salt, purification of rock salt in washing plants may be the economical alternative to a thermal refinery.

OBTAINABLE PURITY IN THERMAL CRYSTALLIZATION PLANTS

If the purities obtainable in washing plants are not sufficient for the intended purpose, more complex processes must be taken into consideration.

Without doubt, the highest degree of purity in the processing of crude salt of any origin can be obtained by removal of the impurities in the brine by chemical precipitation, separation of the precipitated products and subsequent crystallization of the salt from the solution thus purified (Fig. 11). This method requires a high expenditure in terms of equipment and eventually for the use of chemicals and additionally requires the disposal of the precipitation products. It is possible, however, to obtain a very high NaCl quality even without brine purification by applying the purifying stages crystallization in conjunction with hydromechanical washing. This method requires particular stages for the separate crystallization of the calcium sulphate and its separation.

Figure 12 (Messing, 1971; Wöhlk and Messing, 1975; Bauschlicher and Wöhlk, 1985) shows the typical Ca⁺⁺ and Mg⁺⁺ contents in the product of such a plant, in this case for a longer-term operating period. The salt produced in this plant will be used for the chlor-alkali electrolysis and as edible salt.

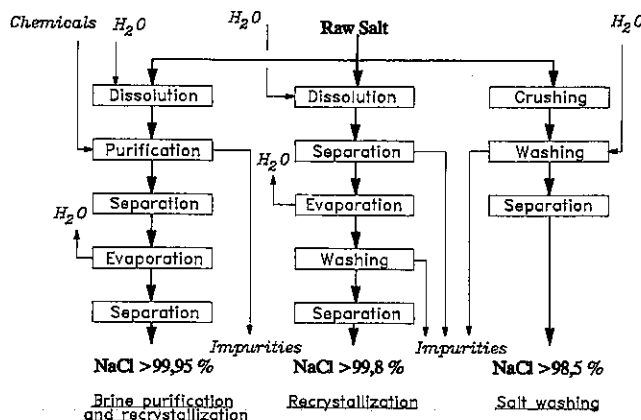


Fig. 11. Different processes for salt production from raw salt.

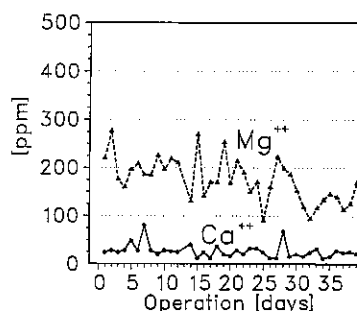


Fig. 12. Salt composition. Evaporation without brine purification.

COMPARISON OF THE TWO PROCESSES AS THE CONCLUSION

The decision as to which process to choose as the optimum one for the salt production will eventually be determined by the intended use and the specific costs for energy and chemicals. If an exactly defined particle shape or size is desired, the product will have to be produced by crystallization. As an example Figs. 13a and b show the different particle shape of a vacuum salt produced in a plant located in Abu Dhabi and a ground washed salt from a solar pond in Venezuela. On the other hand, it is possible to produce a high-quality edible salt in a low-priced hydromechanical salt washing plant. Furthermore, a hydromechanical salt washing plant is definitely suited as the pre-stage upstream of a brine purification for the electrolysis as this will considerably reduce the costs for chemicals. The merits of a hydromechanical salt washing plant are its simple, reliable design and its low energy consumption required for a purity of 98.5% of NaCl. The drawbacks are the limited salt purification and the fact that this process allows only little influence on particle size

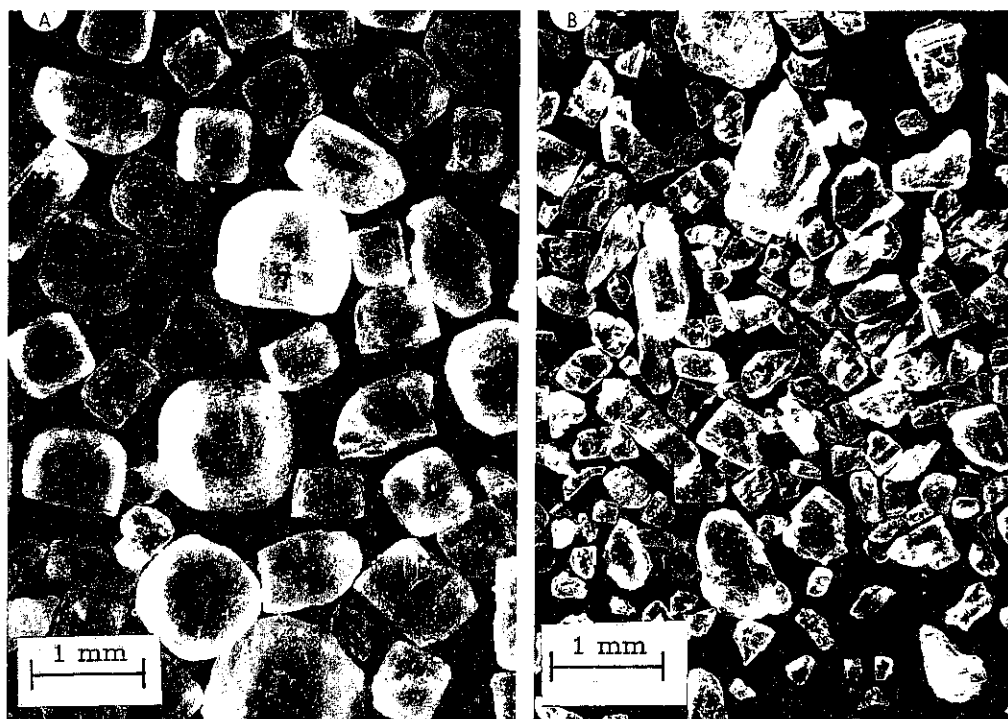


Fig. 13. A. Salt from crystallization plant (Abu Dhabi). B. Salt from washing plant (Venezuela).

(size reduction only), particle shape and colour.

With a thermal recrystallization process, on the other hand, it is possible to obtain any degree of purity with a wide scope of influence on size, shape and particle-size distribution. The products are completely colourless. For these advantages a higher capital expenditure and a higher energy consumption have to be taken into account.

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