Saltworks Engineering

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ABSTRACT

This paper deals with some recent developments and specific procedures in salt works engineering. Following a brief introduction the status of development and design of evaporator-crystallizers with emphasis on hydraulics and crystallization-phenomena is given. Process selection, effluent and by-product recovery, as well as parameters affecting product specifications, are discussed. For reduction in energy consumption, re-use of waste heat, etc., reference is made to current reviews and symposia where this important subject is covered extensively.

INTRODUCTION

The design of salt works is based on

- kind of raw material
- product specification
- production capacity
- facilities
- specific local conditions
- operation economy.

Optimum design of the plant is achieved by balancing capital investment against operating and maintenance costs, whereby low energy consumption is important and receives wide coverage in papers and publications.

There is a rising interest worldwide for thermal recompression, MVR, also combined with multiple effect and heat recovery.

The introduction of MVR in salt plants goes back to 1922-23 when Escher Wyss built the first evaporator-crystallizer applying this system (salt production capacity approx. 300 kg/hr, resp. 1000 kg/hr evaporation).

YESTERDAY'S DEVELOPMENTS—TODAY'S EXPERIENCE

In modern salt works MVR evaporators cover capacity ranges of up to 40 metric tonnes/hr salt production, i.e., 120 metric tonnes/hr evaporation per individual crystallizer.

It is neither the objective of this paper to go into details, nor to repeat what has been presented and published before regarding MVR (Winkler, 1978; Walter and Kondorosy, 1975; Kondorosy, 1980; Rozycki, 1974; Wölk, 1981; and Pavlik et al., 1978).

Meanwhile, important developments have taken place—the new achievements, combined with operational experience, brought further elements into design and layout of salt works. Reference is made to Asselbergs and de Jong, Mersmann, and de Jong, who published a more general survey on the status of crystallizer design.

These innovations are exemplified under headings, such as

- brine purification
- mother liquor recycling and by-product salt separation
- hydrodynamics of suspensions and hydraulic transport design
- crystallizer type and control of CSD, (Crystal Size Distribution)
- effect of vaccination and additives on incrustations and crystal shape
- granulometry and purity of product crystals
- classification and mechanical solid/liquid separation
- drying techniques and product handling
- materials of construction, corrosion/erosion phenomena.

This paper focuses on some of these recent developments and presents a selection of examples.

GRANULOMETRY

Various applications require different salt granulometries. Thus, questions of the following nature might arise:

- To what extent can the granulometry be adjusted in an existing plant?
- What kind of equipment is recommended for obtaining different CSDs?

The answers, generally, are

- an increase in suspension density and prolongation of residence time will result in coarser crystals;
- excessive supersaturation will, to a limited extent, produce more fines but also favours the formation of incrustations.

Supersaturation, however, is not a very suitable parameter to work with in an existing plant, because the crystallizer will be designed for operating within a narrow range and little freedom of variation, in general, is left. Other means, such as dissolution of fines, may be applied for the purpose of increasing the average crystal diameter.

In order to reduce the average crystal diameter, the practical approach is to increase the number of nuclei in the boiling zone by addition of seed crystals. The following example illustrates how effective such a small modification can be.

Operating an industrial crystallizer in the range of 23 to 38 mt/hr salt production, crystals with an average diameter $\bar{d} = 500 \div 600$ μm are obtained. Injection of up to 1.7 wt% of salt dust from dryer cyclones ($\bar{d} \sim 80$ μm) brings the average diameter down to ~325 μm.

The fines from the cyclone outlet are collected in an agitated vessel (~2 m^3) and suspended in preheated brine. The suspension containing approximately 10 to 50 g/l of fines is fed at a constant rate to the evaporator/crystallizer in the external circulation loop (Figure 1).

The result of the addition of seed crystals to a crystallizer system must be considered as specific for the examined system (Figures 2 and 3). A rough estimate of the number of seed crystals, required for reducing the average crystal diameter from 500 to 350 μm, shows that only a fraction of the injected fines is effective. The estimate is based on the following assumptions:

- Crystals are similar in size and in growth rate
- Feed rate and slurry density at injection point are constant
- Brine saturation or undersaturation do not change substantially during the test period

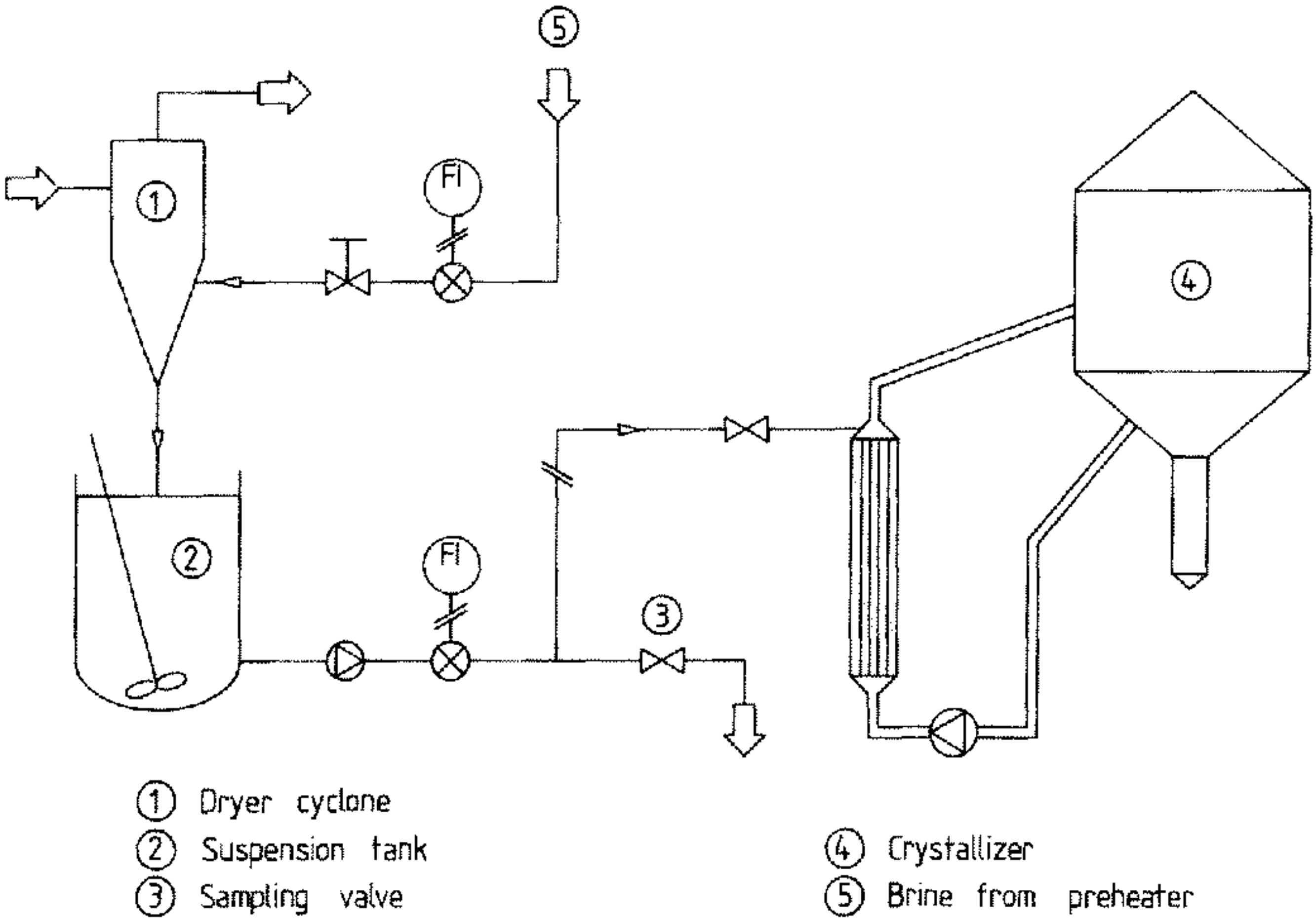


Figure 1. Flow sheet for germination tests.

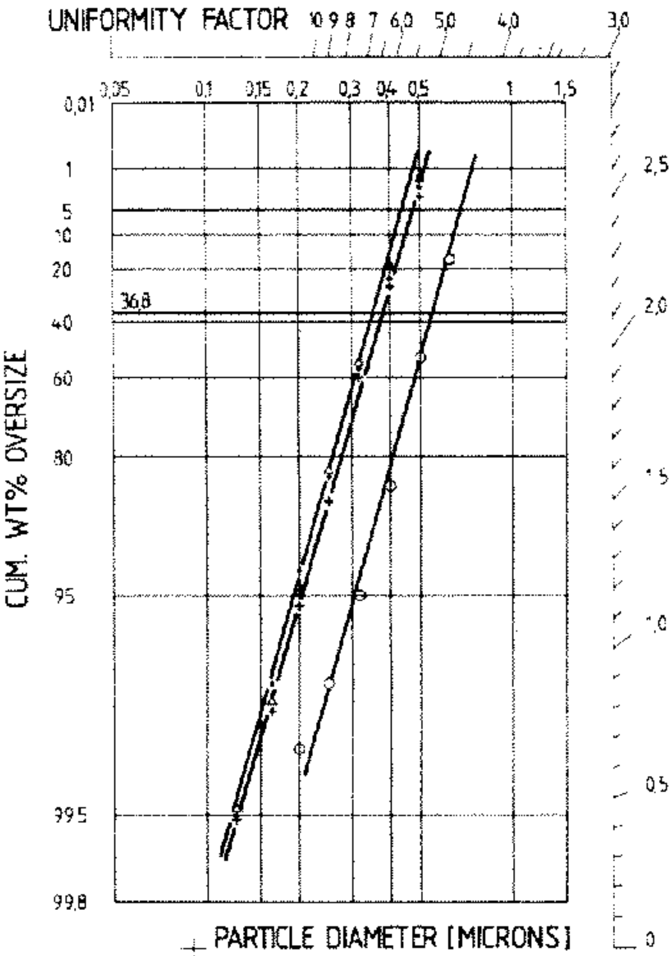


Figure 2. Granulometry obtained with and without seed crystals.

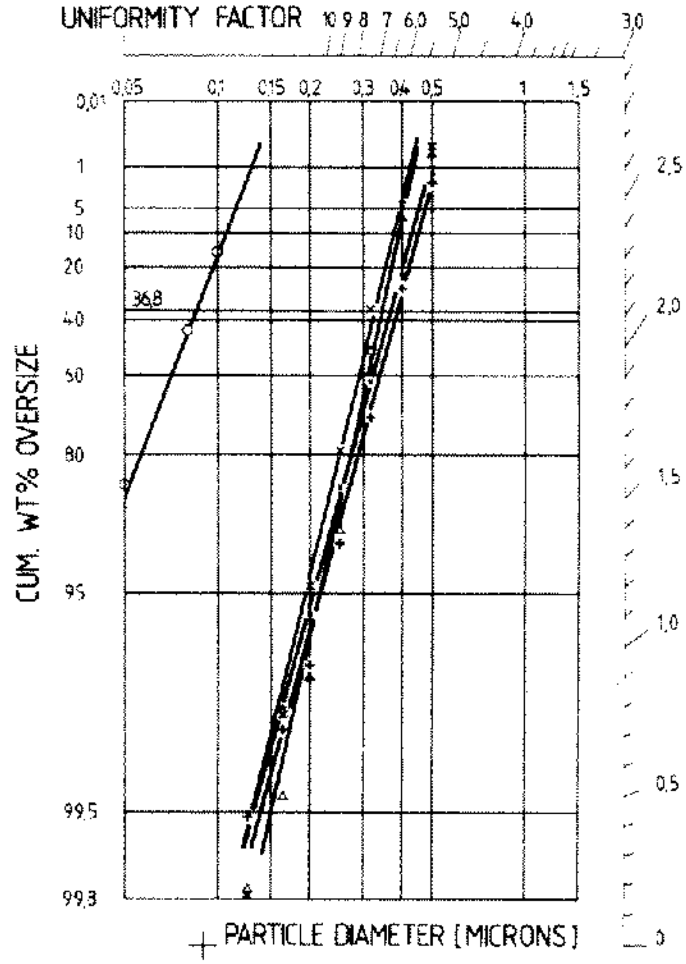


Figure 3. Granulometry of seed crystals and test results.

- Mixing at injection point is fast and thorough
- The suspension is well mixed in the boiling zone
- Evaporation and flow pattern in the boiling zone are regular
- Dissolving is most effective with finest fractions
- Dissolving is poor with large fractions.

At a salt production rate of 32 mt/hr, approximately 320 kg/hr of fines are required (Figure 4). The theoretical mass of crystals, in relation to various diameters, is plotted (Figure 5). It can be observed that injection of the said amount of seed crystals corresponds to a diameter of approximately 85 μm, which is very close to the average seed diameter, as given in Figure 3.

Although the dust contains about 50 wt% of lower fractions, part of which are dissolved and others not becoming effective, the average crystal diameter is, in fact, a suitable parameter for describing the mass of active seed crystals.

An increase of the average crystal diameter is achieved either by prolongation of the residence time or by elimina-

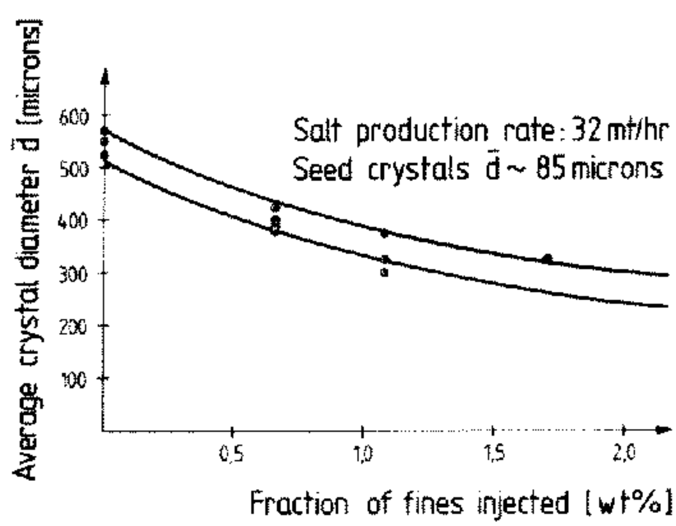


Figure 4. Average crystal diameter as a function of fines injected.

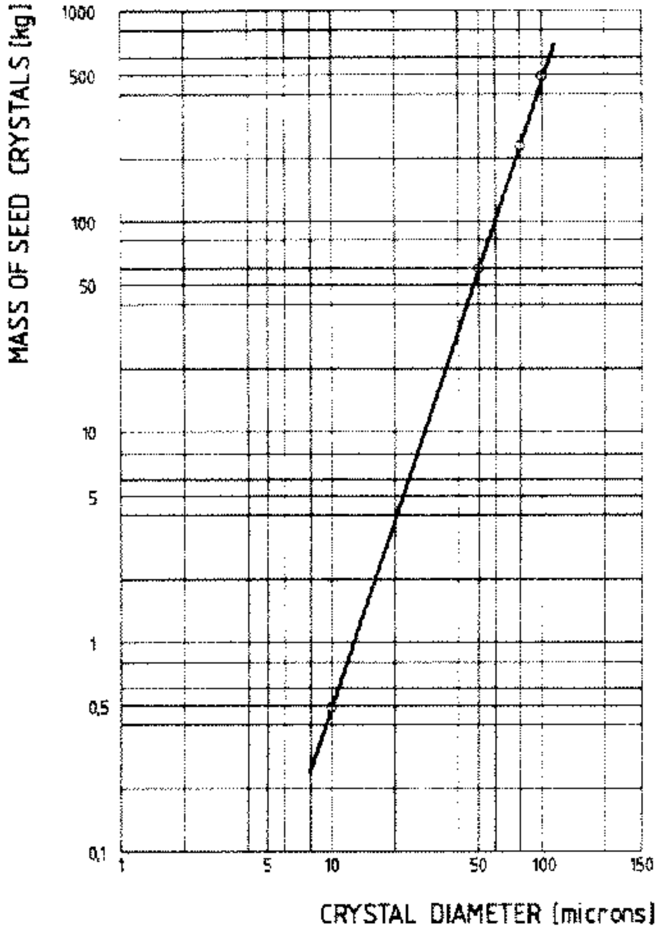


Figure 5. Mass of seed crystals as a function of the crystal diameter.

tion of fines with prejudicial consequences on production rate.

The following example from another salt plant shows a corresponding interaction on average crystal diameter.

Partial elimination of fines brought the average crystal size from 500 up to 700 μm, provided the slurry concentration was kept in the range of 20 wt%. Typically round-shaped crystals are shown in Figure 6.

The origin of unsatisfactory final product CSD and undesired dust formation is not necessarily to be found exclusively in the crystallizer. Unsuitable handling of the product might equally be the cause for abrasion and crystal break-up.

A previous paper (Kratz and Hoyer, 1981) illustrates how subsequent process-steps may affect final product granulometry, especially in the case of abrasion-sensitive crystals.

Because sodium chloride crystals are not very sensitive to handling, the granulometry will mainly depend on the design and mode of operation of the crystallizer in question. Nevertheless, centrifugal pumps for slurry transport, centrifuges and dryers, as well as conveying systems, must be carefully selected. Crystal breakage in modern pusher centrifuges has likewise been considerably lowered, thanks to special high performance designs.

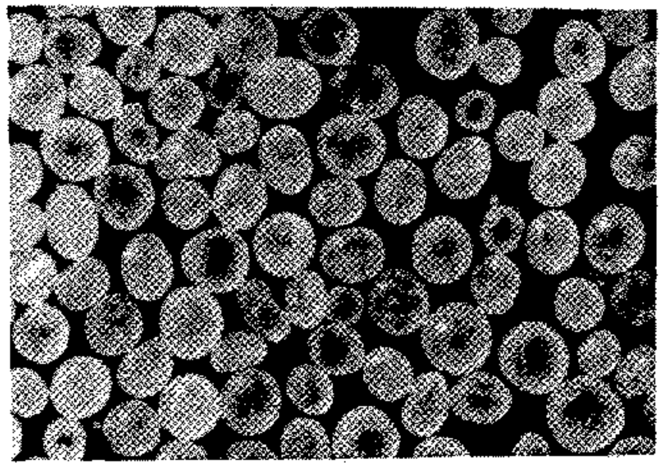


Figure 6. Typically round-shaped crystals.

So, to obtain coarse crystals ($\bar{d} > 600\ \mu m$), special measures must be taken for avoiding breakage in the crystallizer, build-up of excessive supersaturation, irregular flow conditions, and to ensure steady and continuous product discharge.

Classified separation of fines (such as $CaSO_4$-slurry) by means of elutriation is an approved technique. Extra classification is rarely required because the design of crystallizers usually assures uniformity of CSD. Excessive elutriation, as well as unsteady operating conditions, however, may lead to an accumulation of fines and call for occasional extra elimination.

Tests and results, which led to modifications of the Oslo crystallizer, have been described, e.g., by Witte and Voncken, 1971, and by Messing and Hofmann, 1980. These systems avoid magma circulation, and thus the crystals are grown in suspension, unaffected by collisions with the blades of the helical pump. Yet, these systems have some important disadvantages, such as unstable flow conditions and a tendency for incrustations, owing to low seed concentration in the supersaturation zone.

For special purposes and adapted in particular to abrasion sensitive crystals, the Double Propeller® Crystallizer was developed. Recent test work in pilot plants and production units gave evidence of the suitability and economic performance of this type of crystallizer for medium production capacities of coarse grade salt. Crystals formed in the D.P. Crystallizer are about 1000 μm in size and show only slight effects of abrasion (Figure 7). Figure 8 gives the corresponding granulometry. A determined range of CSD is covered by the D.P. Crystallizer with its unique system of matching internal and external circulation. Ideal hydraulic design of the double propeller permits low tip ve-

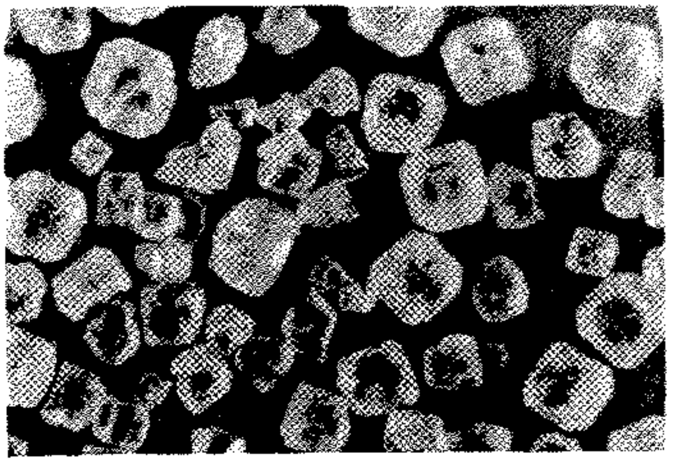


Figure 7. Crystals obtained in DP-crystallizer.

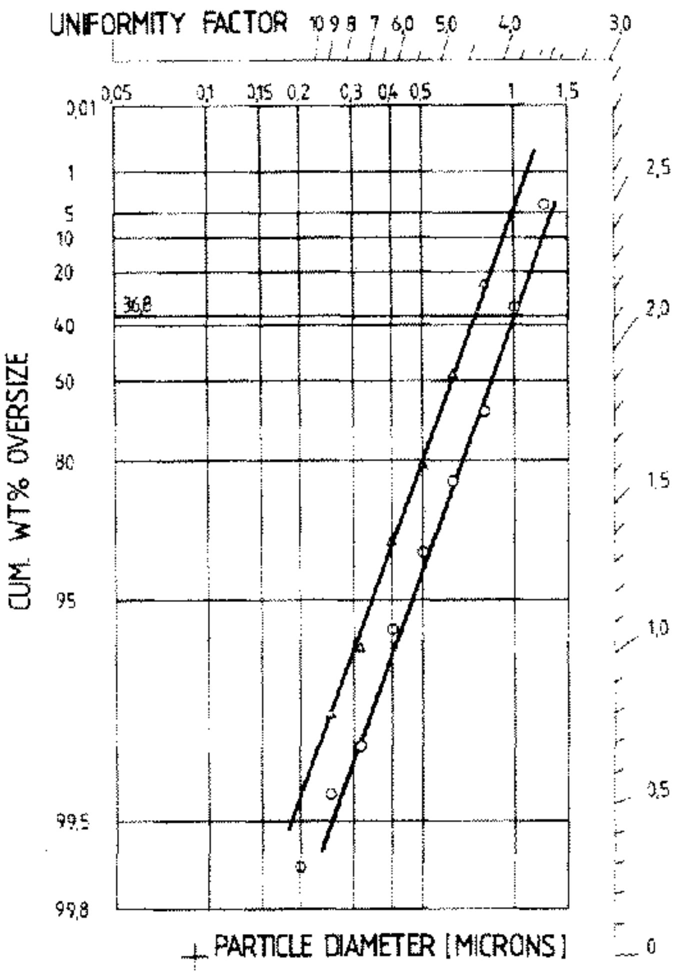


Figure 8. Granulometry of crystals obtained in DP-crystallizer.

locities and ensures a minimum of secondary nucleation, originating from collision with the blades. Practical limits are set, however, by the difference in densities of crystals and mother liquor and corresponding energy input in order to maintain the coarse crystals in suspension.

BRINE PURIFICATION AND RECYCLING

Crude salt and natural brines contain impurities of various compositions and concentrations which lead to crust formation in heater tubes and evaporators and affect the refined salt purity. Hence, brine purification by chemical treatment and separation of the precipitated impurities, such as $CaSO_4 \times 2H_2O$, $CaCO_3$, $Mg(OH)_2$, are in frequent use.

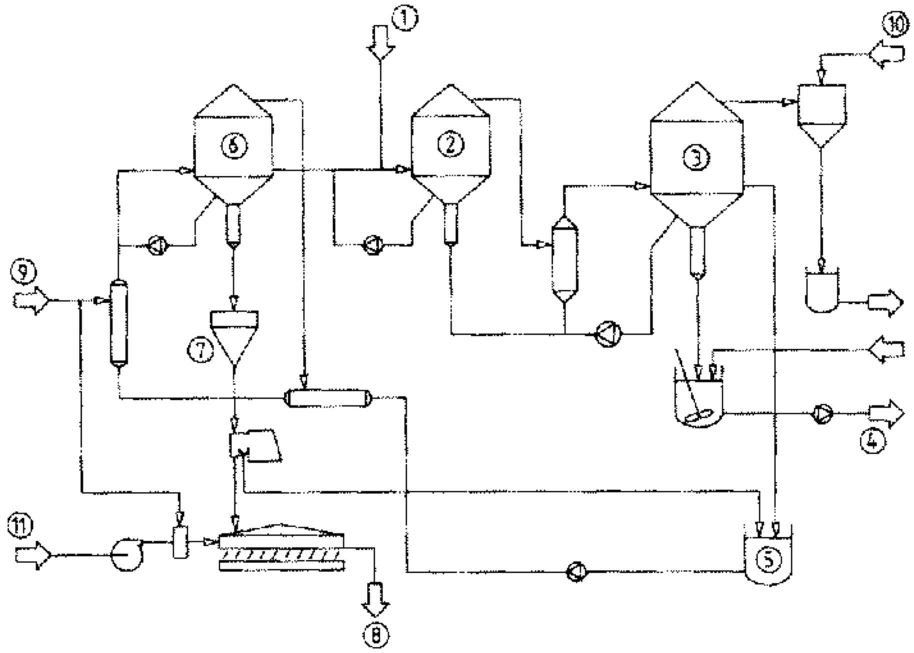
Depending on the concentration and ratio of impurities, like SO_4^{2-}, Ca^{2+}, Mg^{2+}, etc., the chemical treatment will differ from case to case. Soluble salts, i.e., Na_2SO_4, $CaCl_2$, KCl, etc., remain in the purified brine. Consequently, when a certain concentration level is reached in the crystallizer, they have to be purged so they cannot affect product purity. Purging, however, results in considerable loss of NaCl and may cause environmental problems. Various methods of processing such waste streams are available, as shown by the next examples (Van der Stegen, 1978):

Classical separation of sulfates, i.e., by

- freezing out of Na_2SO_4
- precipitation by addition of $CaCl_2$
- recycling of mother liquor to the brine purification, according to system "Schweizerhalle."

Anhydrous sodium sulfate and refined salt of good quality can be recovered in two crystallization stages out of enriched brine. This process makes use of the temperature inverse solubility of sodium sulfate and increases the yield of NaCl. A simplified flow sheet for treatment of a purge stream containing approximately 250 g/l NaCl and 40–50 g/l Na_2SO_4 is shown in Figure 9. The hot mother liquor from the salt plant is flashed down in a first step and concentrated at about 40°C, approximating the saturation of sodium sulfate, whereby NaCl is produced and separated. The remaining mother liquor gets heated up and passes into a flash crystallizer for the recovery of sodium sulfate. The crystal slurry runs through a centrifuge and the humid crystals then move through a fluidized bed dryer before they reach the storage bin. This process and variations thereof yields white, high grade Na_2SO_4.

Other soluble salts, such as KCl, (which cannot be precipitated) can be introduced by the raw brine into the plant. In such case, the latter have to be purged—with undesired side effects—as mentioned before. This can be avoided by recovering crystallized KCl and recycling the brine for production of refined salt. In this process sulfate has to be eliminated as gypsum, while KCl is separated by



(1) Mother liquor from salt plant
(2) Flash evaporator
(3) Evaporator / crystallizer for NaCl
(4) NaCl - Slurry to salt plant
(5) Mother liquor tank
(6) Flash crystallizer for Na_2SO_4
(7) Na_2SO_4 - Slurry to centrifuge
(8) Dryed Na_2SO_4 to storage
(9) Steam to preheater and dryer
(10) Cooling water to condenser
(11) Air to fluid bed dryer

Figure 9. Sodium sulfate recovery process.

cooling crystallization. A serious disadvantage of this method for obtaining KCl may be seen in the high cost of the chemicals required in the preceding brine purification step. Another approach, similar to the first example, has been proposed by Winkler (1982), who recommends avoiding the chemical treatment step. Separation in this case occurs by flash crystallization and subsequent physical treatment of the crystals formed.

REFINED SALT PRODUCTION

The recrystallizer process for refining of solar or rock salt in a closed hot dissolving circuit and subsequent crystallizing by flash evaporation/cooling are successfully applied in order to produce table salt and industrial salt with a purity of over 99.8 wt% NaCl.

Preconcentrated seawater obtained from solar evaporation, salt lake brines and the bleed from desalination plants can also be utilized for the production of salt. The higher the bleed concentration in the preliminary stages, the lower the energy consumption and the capital investment for the supplementary plant. The proportion of other salts, e.g., calcium and magnesium sulfate, resp. chlorides, is normally very high in such brines and chemical pretreatment is often uneconomical.

To prevent scaling of the evaporators and heaters, special measures have to be taken, such as operation with $CaSO_4$ slurry (anhydrite or hemihydrate), addition of surface-active agents or inhibitors, etc., which are apt to modify the incrustation behaviour. Evaporator salt produced from such brines is convenient for human consumption as well as for many industrial applications.

Provided the raw salt is of good quality, i.e., free from sand, stones and shells, etc., washing and milling plants processing solar salt yield a "refined salt" with a purity of over 99 wt% of NaCl.

Other brines, such as effluents from chemical processes with high sodium chloride contents or by-product salts, can be utilized for the production of refined salt by adopting similar process steps.

HIGH GRADE REFINED SALT

Refined salt (evaporator salt) of highest purity (NaCl > 99.9 wt%) is produced from purified brine. This salt is used for chlorine/caustic electrolysis and meets the high standards imposed. The different kinds of electrolytic cells are all sensitive to impurities; the brine, therefore, has to undergo chemical treatment in a very effective purification section. Investment and operating costs for the latter depend largely on the impurities contained in the dissolved salt.

CRYSTALLIZER DESIGN

As mentioned earlier, several authors (Asselbergs and de Jong, 1978; Mersman, 1982; de Jong, 1982; and Schmoll, 1974) have devoted their work to the development and design of crystallizers. In the design of evaporator-crystallizers the general approach is to match hydraulic, evaporation and crystallization parameters. The final product will depend on the type and mode of operation of the crystallizer, the impurities of the brine (mother liquor) and the different ways of handling the crystals.

Evaporators with internal circulation are easier to scale up, whereas flow patterns for tangential inlet and circular flow through the evaporator body are obviously more complex. A stepwise approach, by applying an approved test procedure was found to be useful, i.e., a hydraulic test model serves to determine the basic parameters and their values; these are then scaled-up by "experience factors" obtained from measurements in industrial plants under operation.

The differential pressure Δp, i.e., h_M (water column height) between inlet and outlet of the external circulation loop and the vortex depth ΔH are measured for various flow rates, c, whereas

swirl intensity c^2/D,
dynamic head $(\rho/2) \cdot c^2$,
and the pressure loss coefficient $\Delta p/(\rho/2) \cdot c^2$

are calculated and plotted on a graph.

Examples of various geometrical configurations, such as ratio of inlet tube diameter to evaporator diameter, position of inlet and outlet nozzle are plotted in Figure 10.

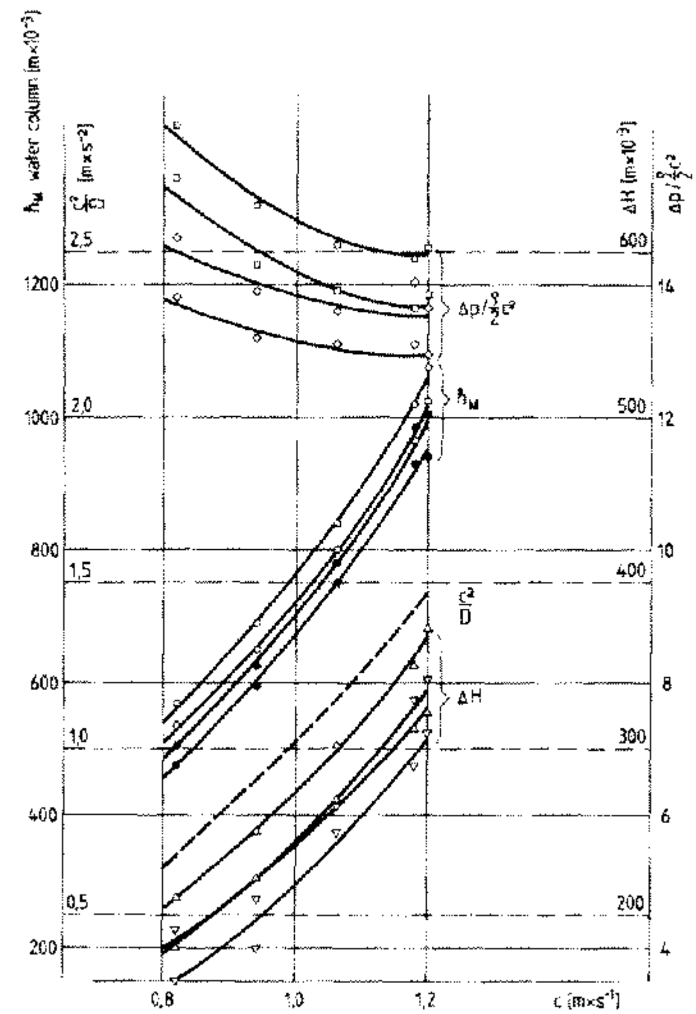


Figure 10. Test results from hydraulic model.

CONCLUSIONS

Important developments, such as vacuum-evaporators, multiple-effect, thermal recompression, and MVR were introduced some 60 to 70 years ago. Today they are the main systems for designing salt plants of minimum steam and energy requirements. New spectacular developments in salt works engineering seem to be non-existant, yet it can be observed that numerous contributions have been tested and approved. We may, therefore, come to the following conclusions:

- Recent developments in salt works engineering result in improvements of details, leading to high performance and product quality and optimum balancing of investment and operating costs.
- Crystallizer design and performance have passed through an age of mystery to established unit operation methods. Many phenomena have been studied, reproduced and classified with the aid of physical and mathematical models.
- Process design, including brine purification and waste stream processing, recycling and by-product salt separation, must be considered under the specific conditions and have reached a level of vital importance with regard to plant economy.
- Pilot plant work for process design and model approach for scale-up of equipment are useful assets in salt works engineering.

The designer of salt plants is obliged to meet the demand and follow the trend of salt manufacturers and consumers by applying the latest technical achievements to future equipment.

REFERENCES

Asselbergs, C. J. and E. J. de Jong, 1978. A study on integral design of salt crystallizers, Fifth Symposium on Salt, v. 2, pp. 233-249. Northern Ohio Geological Society, Cleveland, Ohio.

de Jong, E. J. 1982. Entwicklung von Kristallisatoren. Chem.-Ing.-Tech. *54*, No. 3, pp. 193–202.

Grootscholten, P.A.M. et al. 1981. Effect of crystallizer geometry on crystallizer performance. Industrial Crystallisation. Jančic, S. J. and de Jong, E. J. (ed.), North Holland Publishing Company (1982).

Kondorosy, P. 1980. Modification of existing plants for mechanical vapor-recompression. VDI-Berichte No. 383, No. 442.

Kratz, E. W. and F. Hoyer. 1981. Process steps affecting crystal granulometry, Industrial Crystallization. Jančic, S. E. and de Jong, E. J., (ed.) North Holland Publishing Company (1982).

Mersmann, A. 1982. Auslegung und Mass Stabsvergrosserung von Kristallisatoren. Chem.-Ing.-Tech. *54*, No. 7, pp. 631–643.

Messing, T. and G. Hofmann. 1980. Industrielle Kristallisation—Moderne Grosstechnische Anlagen und Fallstudien Chem.-Ing. Tech. *52*, No. 11, pp. 870–874.

Pavlik, A. et al. 1978. Description and operation of a high capacity evaporator for the production of a very pure chemical grade salt. Fifth Symposium on Salt, v. 2, pp. 335–339. Northern Ohio Geological Society, Cleveland, Ohio.

Rozycki, J. V. 1974. Economics of recompression salt evaporation. Fourth Symposium on Salt, v. 2, pp. 425–431. Northern Ohio Geological Society, Cleveland, Ohio.

Schmoll, E. 1974. Special aspects in the engineering of large evaporation plants for NaCl recovery. Escher Wyss News 1974/2, pp. 2–9.

Van der Stegen, J.H.G. 1978. Principles and economies of salt production and processing. Fifth Symposium on Salt, v. 2, pp. 519–524. Northern Ohio Geological Society, Cleveland, Ohio.

Walter, R. O. and P. Kondorosoy. 1975. Fundamental economic principles in evaporation. Escher Wyss News, 1975/2, pp. 2–8.

Winkler, R. 1972. Recovery of sulphate-loaded discharge brines from salt refining plants. Escher Wyss News 1972/2–1973/1, pp. 3–7.

Winkler, R. 1978. Technologie der Thermokompression im Salinenbetrieb. Fifth Symposium on Salt, v. 2, pp. 397–402. Northern Ohio Geological Society, Cleveland, Ohio.

Winkler, R. 1982. Swiss Pat. Appl. No. 7518/82–5.

Witte, J. F. and R. M. Voncken. 1971. Two Case Histories in the Design of Crystallizers, Brit. Chem. Eng. *16*, No. 8, pp. 681–685.

Wölk, W. 1981. Industrial crystallization under the aspect of energy economic operation, Industrial Crystallisation, Jančic, S. J. and de Jong, E. J. (ed.), North Holland Publishing Company (1982).