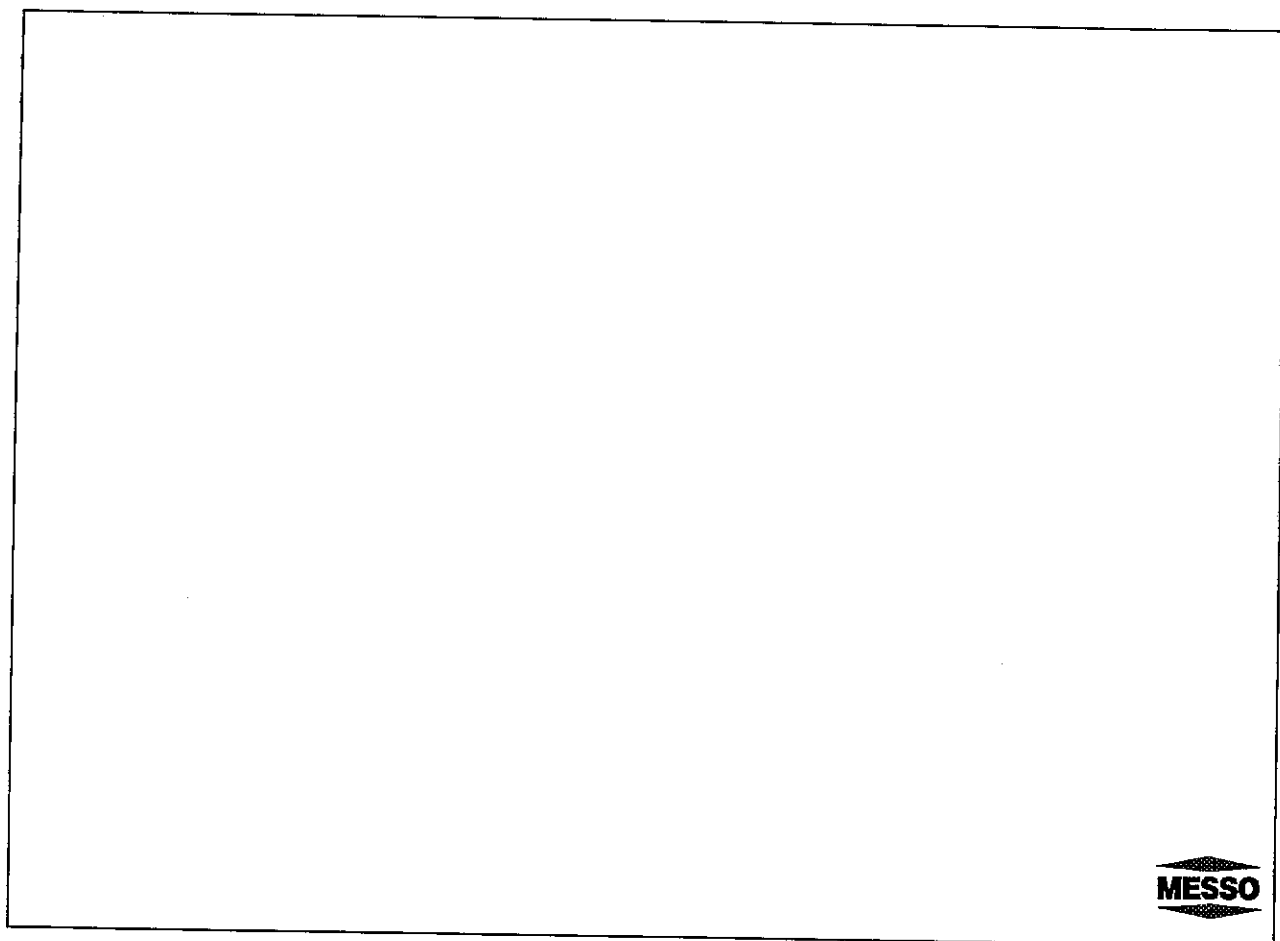


# **Industrial Crystallization Under the Aspect of Energy Economic Operation**

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## Industrial crystallization under the aspect of energy economic operation

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With the increasing costs of primary energy sources the plant owners and plant manufacturers are directing their efforts towards energy efficient plant layouts. Practical case studies are used to illustrate the possibilities by which substantial savings in energy can be achieved. These measures range from relatively simple operational or design changes in plant techniques and process technology to alternative processing concepts and alternative energy sources. The technological parameters of crystallization have to be taken into account in all energy optimization steps. In this context the application of mechanical vapour compression to crystallization plants is also discussed.

The plenary lecture in the section Industrial Crystallization during the 7th International Symposium [1] dealt mainly with the selection of suitable crystallizers and crystallization processes with regard to the criteria: production of a definite crystal size distribution and achievement of a definite purity specification.

This concept is being extended in this contribution so as to include energy efficient operation of crystallization plants.

With rapidly increasing energy costs the efforts of plant owners and plant manufacturers are directed to-day in general towards optimal energy utilization.

In times when energy costs did not dominate in the total cost calculations the choice of the system or process could be carried out solely on the basis of low investment costs or on the basis of simplest possible operation. In contrast to this the decisions these days relating to investment should take the future energy prices into consideration. The present tendency thus leads to higher investment on energy saving systems than would be justified by economic considerations as dictated by the to-days energy prices. In spite of the stretched energy situation it is not justified that the dimensioning of the plants should be carried out exclusively to achieve an energy minimum. Even to-day the plant which delivers the required product at a minimum of over all cost is the right one.

Although many chemical processes can be

optimised purely on the basis of energy considerations, in planning and operation of crystallization plants a number of other process characteristics must be taken into account. Thus the working temperature, temperature gradients, the volume of the apparatus etc. are closely related to the kinetic data of the crystallization system and in certain cases can be varied only within very narrow limits. On the other hand attention must often be paid to scaling tendencies of the system. It is thus possible to think of cases where the plants to achieve an energy minimum can not be realised on account of system properties and parameters. Usually of course it is quite possible to realise remarkable energy savings even after taking into account the specific circumstances which effect the crystallization. These savings result from an energy conscious plant operation and plant design.

The ways of energy savings are manifold and range from relatively simple measures to new constructions and alternative processes:

### 1. Improvements in design and operation

#### 1.1 Increasing the operational availability

- timely and planned maintenance
- avoidance of crust formation by problem orientated design, construction and operational measures

#### 1.2 Avoidance of excessive quality product requirements

### 1.3 Improvement of heat utilization in the process as a whole

- utilization of the heat of condensates
- number of stages in the plant
- heat recovery

### 1.4 Control of the solvent (water) economy

- avoidance of excessive washings

## 2. Energy savings by alternative schemes

### 2.1 Alternative processes

- flash processes

### 2.2 Alternative energy sources

- thermocompression

Many of the points raised above need not be explained. Ideas like the preheating of solutions and utilization of the heat capacity of condensates are well known and practised.

Some newer concepts for energy savings are illustrated by examples below.

### Increasing the operational availability of the plant

The on line time of crystallization plants is often limited by crust formation. The necessary cleanings mean a loss of production due to interruption of the operation and the added washing water has to be evaporated again. This leads to the demand that crystallization plants should be so designed, that scaling and deposits in flow sections should be avoided as far as possible.

As a result of suitable constructional changes in Oslo-crystallizers, which are especially prone to scaling [2] the on stream periods can be increased from a few days to some weeks [3].

In the Oslo-crystallizer of known design the circulating mother liquor is clarified by sedimentation in the external chamber of the crystallizer (Fig. 1). In case of evaporation crystallization this almost crystal free mother liquor is heated up in the heat exchanger and so in most cases it becomes undersaturated. In the evaporation chamber evaporation takes place. The resulting supersaturated solution flows downwards within the central pipe and after redirection it streams through the salt bed. The supersaturation is reduced on the surface of crystals which are presented here.

In this system all those areas are in danger of incrustation where the supersaturated solution is flowing. These are, the upper evaporator chamber, the cone and the central pipe. If the crusts drop off and block the ring space of the bottom the bed of fluidized crystals may collapse. This involves periodical stoppages and extensive cleaning.

The on stream periods for this type of crystallizer vary between 4 days (NaCl) and 4 weeks depending upon the substance.

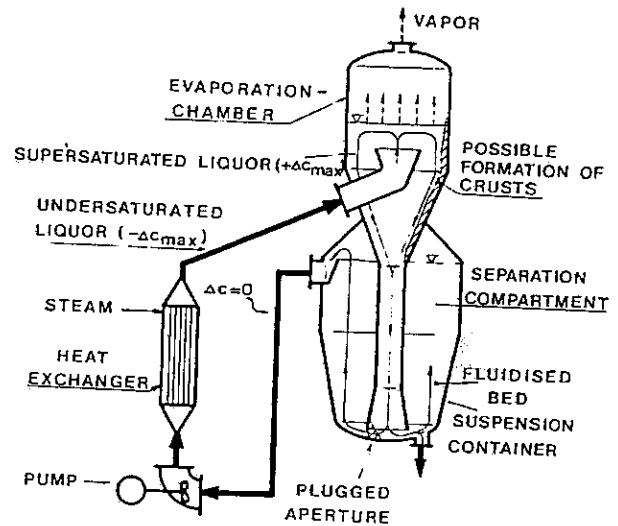


Fig. 1: Conventional OSLO-Crystallizer

By means of a new construction which takes this into consideration it has been possible to mitigate the problem. The outstanding feature of this new design (Fig. 2) is the reversal of liquor flow in the evaporator chamber of the Oslo-crystallizer. The undersaturated solution flowing out of the heat exchanger is fed from below into the evaporating cone. This means that now the undersaturated solution is continuously flowing around the evaporating cone and the outer wall of the evaporator. These parts were previously especially prone to crust formation. At the liquid surface the superheated solution expands and so flows in a supersaturated state through the central pipe into the crystal bed. Compared to the traditional construction the retention time of supersaturated solution in the evaporator section has been reduced significantly. By this change the scaling tendencies have been diminished greatly and the on stream time increased. In case of NaCl operation times of more than a month

have been achieved.

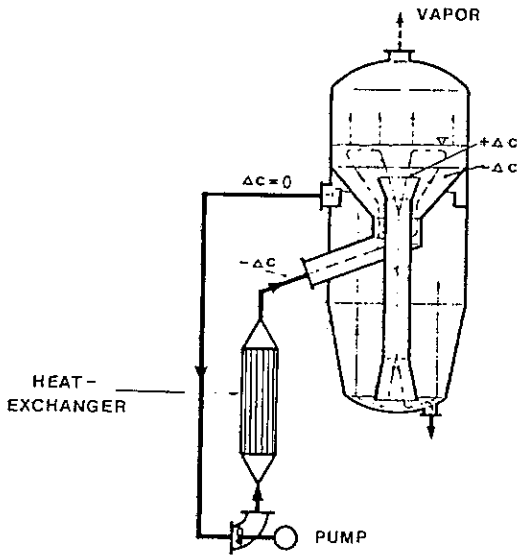


Fig. 2: Modified OSLO-(MESSO)-Crystallizer

Apart from such purely constructional measures it is often essential to carry out technological changes in order to avoid crust formation.

A classical example for this is seen in the operation of salt plants where in many cases depending upon the raw materials calcium sulphate precipitates during evaporation crystallization. This regularly leads to crust formation on the heating surfaces.

A practice which has proved to be effective since some years involves holding so much calcium sulphate in suspension in the circulation liquid that the surface of these crystals is large enough to keep the calcium sulphate supersaturation at a low level. So desupersaturation takes place at the  $\text{CaSO}_4$ -crystals and not on the surfaces of the heat exchanger tubes.

Beside this surface reaction the circulating  $\text{CaSO}_4$  suspension at relatively high velocities has an abrasive effect which plays an effective role in avoidance of incrustations.

New investigations [4] show that the hydrate structure of the crystallised  $\text{CaSO}_4$  has an important influence on the crust formation. In spite of sufficient seeding with the crystallizing compound, crust formation on the heat exchanger tubes is observed after longer operating periods in case of calcium sulphate dihydrate crystallization. It was found

that crust formation can be completely avoided if it is possible to crystallize calcium sulphate hemihydrate instead of dihydrate. Naturally in case of these crystals the suspension density should also be held sufficiently high.

The reason for this difference in scaling behaviour lies obviously in the different growth patterns of the two hydrates.

For the growth of  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  the order of crystal growth has been determined to be 1 which is indicative of a diffusion controlled growth. The corresponding value for  $\text{CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$  is around 2.

In diffusion controlled kinetics the crystal growth is faster when the relative velocity between the growing crystals and supersaturated solution is higher. This value reaches a maximum in the heat exchanger tube after heterogenous nucleation has taken place there. Here the solution streams past a fixed crystal at the rate of about 1.5 m/s. As against this the growth rate of calcium sulphate hemihydrate does not change with the relative flow velocity. Taking these facts into account e. g. plants, where NaCl and potable water are produced from sea water have got a new design. In the common operation where the seawater is fed into the hottest stage (direction of feeding: 1→2→3→4) the hemihydrate precipitates in stage 1 while in the following stages dihydrate crystallizes out because of the concentration/temperature relationships prevailing there (Fig. 3).

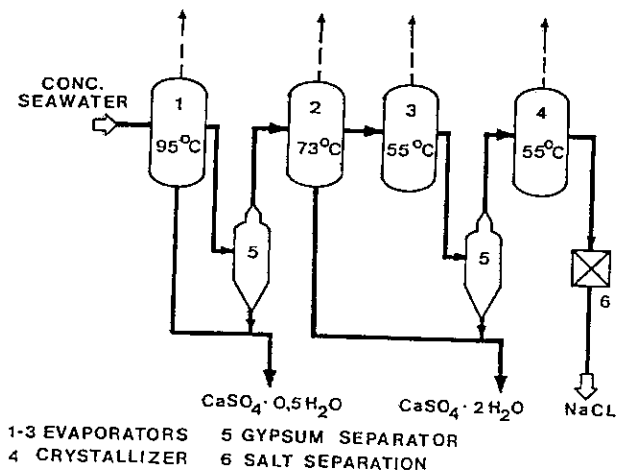


Fig. 3: Flow sheet for NaCl production from concentrated seawater (Crystallization of different hydrates of  $\text{CaSO}_4$ )

Little scaling tendencies still can be seen here due to the diffusion-controlled, that means flow-velocity dependent growth.

A technological alternative to this system comprises of a plant arrangement in which only  $\text{CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$  crystallizes in all stages (Fig. 4).

to be added and subsequently has also to be evaporated again. A critical examination of the requirement for producing especially large crystals can lead to saving of large amounts of steam and cooling water.

In case there is a real need for large crystals then fines dissolving should be reduced as much as possible by adequate designing the plant, that means for example by minimising the mechanical attrition, abrasion and secondary nucleation. This is achieved by selecting suitable pumps and separating systems. As a rule one should always use slow running machines in these cases. Although this results in higher investment costs these are generally ammortised quickly by lower operating costs.

Avoidance of excessive water addition in the plant

It is quite common to carry out preventive washing in crystallizers which increase the production safety. However, excessive care can sometimes be carried to such extremes that product losses occur which necessarily leads to increased energy consumption. A very simple example may explain this statement:

To rid a crystallizer wall of crusts a wash ring commonly is used (Fig. 5).

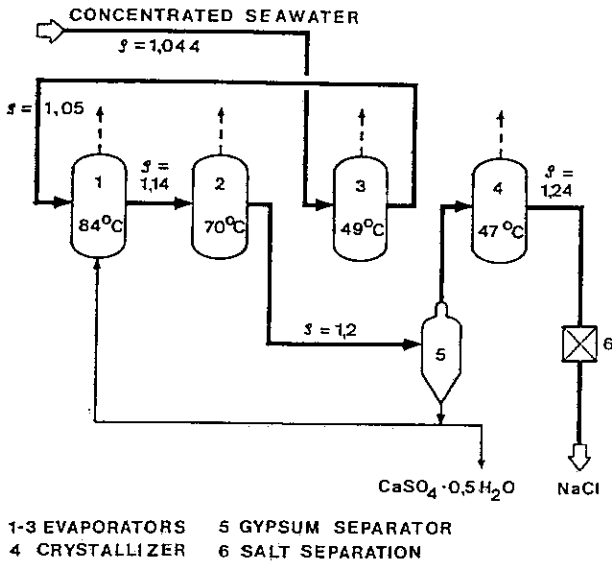


Fig. 4: Flow sheet for NaCl production from concentrated seawater (Crystallization of only  $\text{CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$ )

In this plant the direction of feeding of the stages has been chosen according to the prevailing existance range of the hemihydrate modification (3-1-2-4). In-crustations of  $\text{CaSO}_4$  are not observed in such plants. This results in a saving of 800 t/a of steam for each ton of sodium-chloride produced per hour.

Avoidance of excessive quality requirements of the product

The product specifications naturally have a high priority in determining the choice of the most suitable process. However when setting these specifications one must keep in mind that excessive quality requirement can possibly lead to disproportionately higher investments or energy consumptions. As an example mention is made of excessive requirements relating to crystal size distribution which in certain cases can be arrived only by an additional dissolution of fine crystals.

In vacuum cooling crystallization or surface cooling crystallization, heat for example in form of fresh steam, has

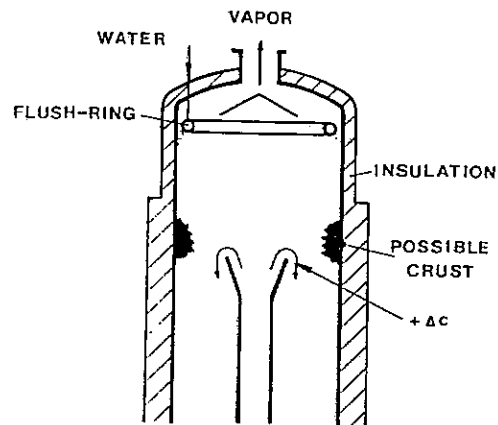


Fig. 5: Vapour chamber in evaporation crystallizers

By frequent flushings - each just for a few seconds-deposits in the vapour chamber can be definitely kept down by this means. However in a middle sized

plant (for example a 4 stage crystallization plant with evaporators having 4 m diameter) each minute of unneeded washing results in extra steam costs of about DM 18 000,-- per year. Similar effects result from negligent maintenance of the stuffing boxes on pumps. If due to leaky seals the rate of sealing water has to be raised by only 20 l/hour then this results in costs of DM 14 000,-- per year for the extra steam consumed. For purposes of process control the installation of water meter in sealing water and washing water lines is recommended for this reason.

Improvement of heat utilization

In regard to this problem it was established in the introduction that these days the energy prices dictate that best possible layout for plants be chosen already at early planning stages. Measures for utilizing process waste heats, for example in preheating the solution with vapour condensate have become selfevident.

The consideration of the number of stages of plants has taken on a new dimension because of energy costs.

In the optimisation of plant concepts for evaporation processes the number of stages is always accepted as a marginal condition. For vacuum cooling crystallization plants criteria other than minimizing of steam consumption were mostly the determining factors in design considerations.

The vapours arising out of vacuum cooling crystallizers are in many cases condensed with cooling water so that they are lost as a heat source. By a heat recovery system this waste heat can be usefully employed. This technique is used with success in an exemplary by the potash industry to reduce the operation costs of the potash crystallization drastically (Fig. 6).

In this process raw salt, consisting of KCl, NaCl and a number of other salts is dissolved at around 100 °C. The solution is held in such a state of equilibrium with the other salts that KCl is dissolved preferably.

By cooling this solution to 30 °C potassium chloride is crystallized. The cold solution has a composition which is suited for dissolving the raw salt. For this use it must be reheated.

To save energy the cold mother liquor is fed into surface condensers in which the vapours arising out of the vacuum cooling are condensed. It is obvious that more heat can be recovered if the number of stages in cooling crystallization and for heating the mother liquor is increased.

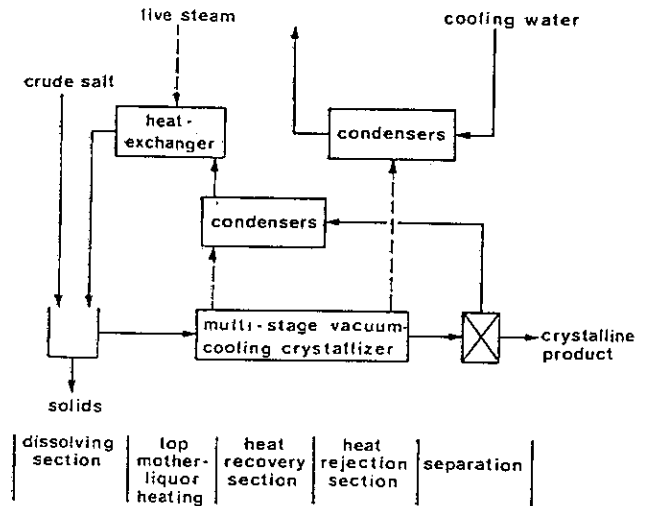


Fig. 6: KCl-crystallization plant operating-diagram

As against this with increasing number of stages the investment costs also increase.

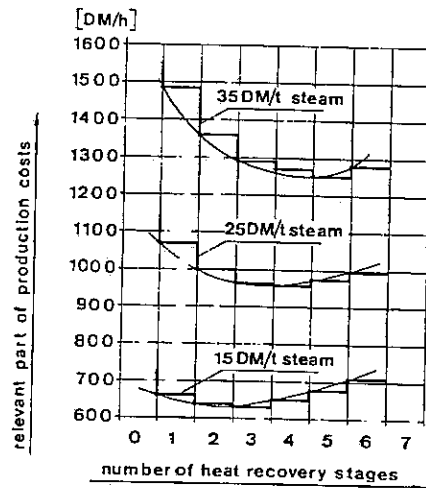


Fig. 7: Production costs over number of heat recovery stages

In Fig. 7 the production costs relevant to this consideration for 100 t/h KCl are plotted against the number of stages with the steam price as parameter. With higher steam prices an increase in the optimal number of stages is observed. To elucidate the importance of selecting the right number of stages let us assume

that two instead of three heat recovery stages are chosen, at a steam price of 25,-- DM/t. This would increase the annual production costs by around 300 000,-- DM.

In such plants the dimensioning of heat exchangers in the heat recovery part is especially important. By correspondingly large surfaces small temperature differences between the condensing vapours and the mother liquor to be heated can be realised.

Direct contact condensers should be used whenever this is permitted by the water balance. Contrary to surface condensers in this type the achievable temperature of mother liquor is determined by equilibrium vapour pressure which means that higher end temperatures are reached in case of direct condenser operation (Fig. 8) [5].

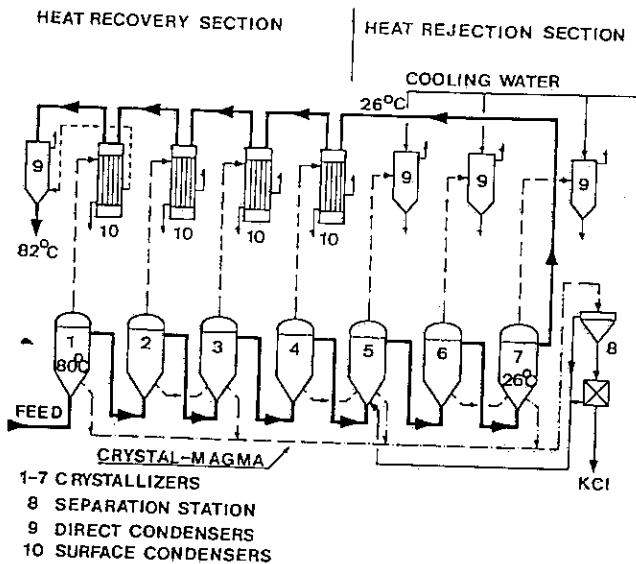


Fig. 8: KCl-cooling-crystallization with heat recovery

In the plant under discussion here each degree increase in temperature of the solution results in annual savings of DM 220 000,-- for each 100 t/h KCl

Alternative processes

When planning new crystallization plants, all measures discussed up till now should be considered in the early designing stages. Further the crystallization process should be seen as an essential planning factor. Usually the process (evaporation, cooling, vacuum cooling etc.) is determined by the solubility properties of the product which is being crystallized.

The first selection criterium is: for low temperature gradient of saturation concentration evaporation-crystallization should be carried out and with higher temperature dependance of saturation concentration cooling crystallization should be used.

With the example of common salt crystallization it can be shown that some favourable processes can be found when one takes a broader point of view.

In the temperature range from 60 °C to 90 °C the solubility coefficient for NaCl is 0,025 wt. %/K. With this low value, evaporation crystallization is generally used to produce NaCl (Fig. 9).

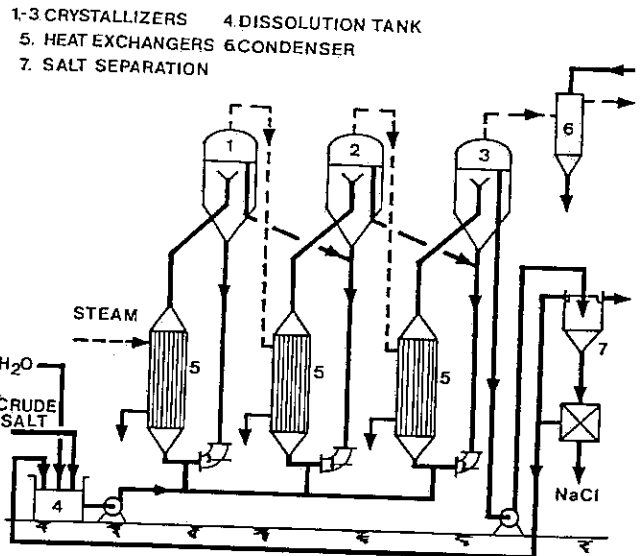


Fig. 9: 3-stage evaporation crystallization for NaCl-production

Starting with a saturated solution 2,7 t of water have to be evaporated for each ton of salt. This takes place in multiple evaporation crystallization plants. Large units have their optimum generally between 4 and 5 stages. For the production of high purity NaCl from raw salt (rock salt, sea salt) - inspite of the low concentration dependance from temperature - the vacuum cooling crystallization process (flash process) can also be used. In Fig. 10 the simplified mass flows for the evaporation and for the flash processes are shown. In case of the flash process the rate of evaporation is less than in case of the evaporation-crystallization (1600 kg against 2700 kg

per ton NaCl) and therefore the amount of heat to be supplied is correspondingly lower.

In heat recovery systems direct contact condensers can be used which results in lower investment costs. In addition, because of the surfaceless heat exchange in most of the plant, the danger of scaling is reduced. This also contributes to energy savings (Fig. 12).

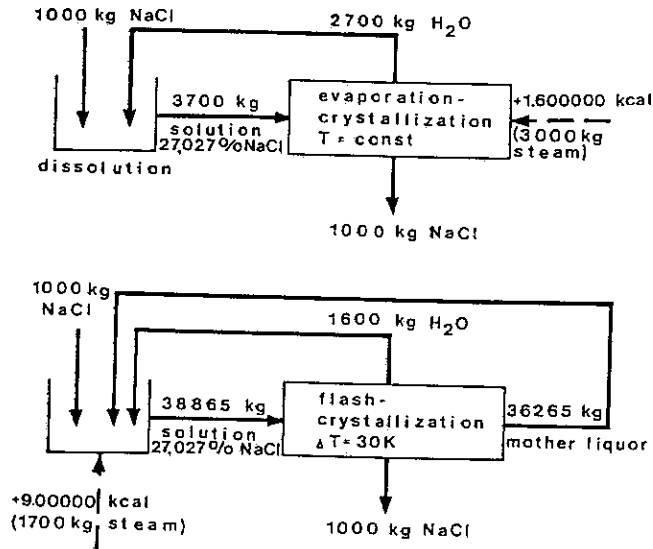


Fig. 10: Mass-balances evaporation crystallization versus vacuum-cooling crystallization

In case of multi-stage system the steam consumption is lower for both processes as could be expected (Fig. 11).

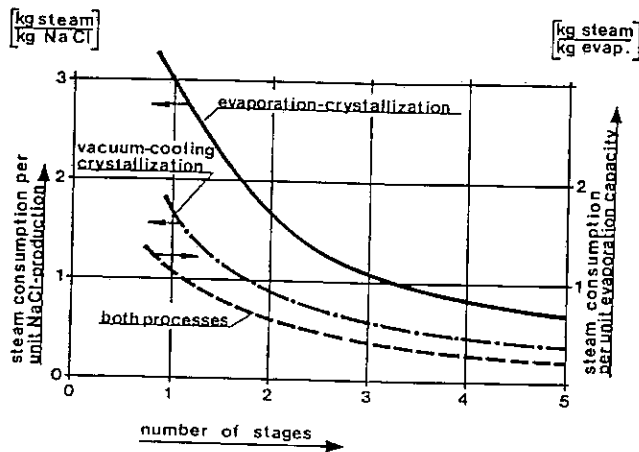


Fig. 11: Specific steam consumption for evaporation and vacuum cooling

Apart from energy savings the application of a vacuum cooling offers numbers of other advantages.

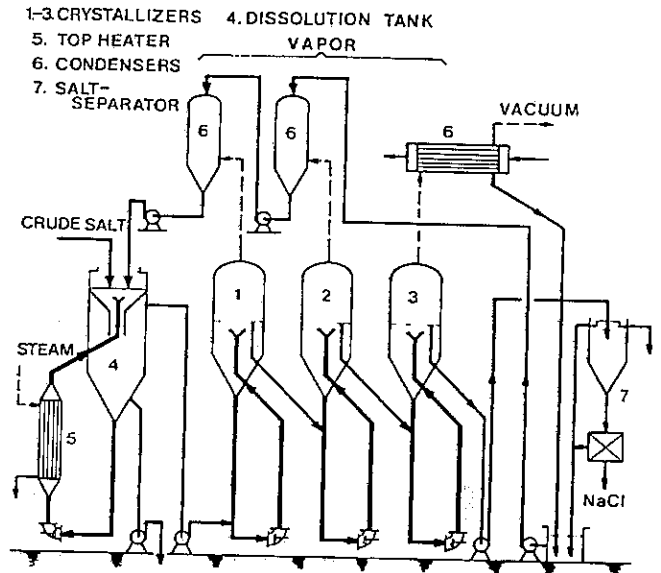


Fig. 12: Vacuum-cooling-crystallization (flash-process) for NaCl-production

As against these advantages there are certain problems which should be kept in mind when selecting the process. The dissolving station is operated at a relatively high temperature (> 373 K). It becomes necessary to take special measures against radiation losses and for the removal of insoluble components of the raw salt in the dissolving station. Further to assure the full production capacity the solution must be fed to the plant in a completely saturated state. This is because each 0,1 % NaCl undersaturation results in a production loss of about 5 %. To have full benefit from this energy saving process it needs a diligent design and operation.

Alternative energy sources

The application of steam jet compressors which are operated by "waste steam", to vacuum cooling crystallization plants is quite common. Evaporation crystallization plants are preferably heated with waste steam and are built multi-stage to increase the economy.

As factory complexes as a whole today are designed for higher energy efficiency less "waste steam" becomes available. So the planning engineer has to look for thermodynamically favourable alternatives for heating the crystallization plants. Such a thermodynamically preferable alternative to steam jet pumps is offered by the use of electrically driven refrigerating machines in vacuum cooling crystallization plants. For evaporation crystallization vapour-compression must be taken into consideration.

As seen from an energy point of view these alternatives are much superior to the customary techniques. However, an exergetic evaluation gives a real picture of the best technology [6]. As for an example of alternative energy sources the application of vapour compression in crystallization plants is discussed and for simplification the price of the different energy forms is taken as a basis for the selection. Whereas in multi-stage evaporation the waste steam of the earlier stage heats the next one and the first stage is fed with fresh steam, the vapour compression employs the evaporation enthalpy of the vapours produced in a stage to heat the same stage. The vapour compressor takes in a heat flow at a lower temperature (evaporation temperature) and raises it to a higher temperature level (heating temperature). These vapour compressors can either be driven by steam or electrical energy. The latter will be discussed in this contribution.

In a greatly simplified diagramme (Fig. 13) of such a thermocompression system it is assumed that the vapour from an evaporator with  $100^{\circ}\text{C}$  has to be compressed to a pressure related to saturated steam of  $110^{\circ}\text{C}$ , so that the temperature difference in the heat-exchanger is sufficient for heat transfer.

For this 24.4 kWh electrical energy for each ton evaporation are necessary. As against this the heat requirements of a one stage evaporator amount to about 690 kW for each ton evaporated. In other words a steam heated single stage evaporator needs 28 times the energy value of a thermocompression plant. This figure makes thermo-compression very attractive.

With increasing boiling point elevation of the solution to be evaporated - at a constant temperature difference for heat transfer - the energy required for thermo-compression also increases. For a boiling point elevation of 10 K, the compressor needs about 50 kWh for each ton water evaporation.

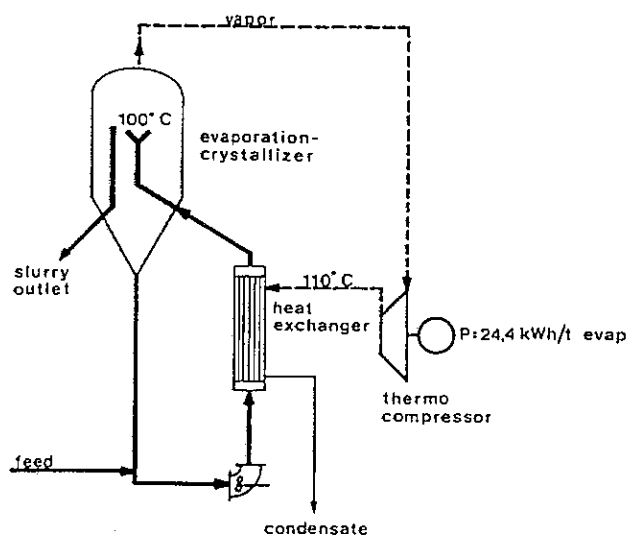


Fig. 13: Simplified operating diagram for vapour compression in an evaporation-crystallization-plant

For an actual comparison one has to weigh thermo-compression against a multi-stage evaporation. If one considers a 5 stage evaporation crystallization plant then the heat requirement for evaporating one ton of water is reduced from 690 to about 160 kWh. The specific costs of electricity and steam give a first idea whether thermo-compression can be chosen or not.

When one continues this comparison, which among others also applies to NaCl plants, with energy prices of 0,10 DM/kWh and 30,-- DM/t steam, one arrives at energy costs of DM 5,-- for thermo-compression and DM 7,80 for the 5 stage plant, for each ton evaporated. In relation to one ton of NaCl these costs are DM 13,50 and DM 21,-- respectively.

For the vacuum cooling crystallization described in the previous chapter the comparative costs are around DM 12,--/t NaCl. Although in this comparison the thermo-compression is energetically the best choice, at the selected energy prices it does not turn out to be most economical choice also. With reduced current price (0,08 DM/kWh the operating costs of thermo-compression are reduced to DM 10,80 /t of NaCl. At this price thermo-compression has the lowest operating cost.

In an exact comparison of course cooling water consumption and investment must also be taken into account. Cooling water consumption is exceptionally low in thermo-compression plants but in general the investment for such plants is higher.

Special attention must be paid to the design of thermo-compression plants. As discussed in the beginning, in planning steam heated crystallization plants special measures must be taken to prevent the formation of crusts thereby ensuring longer running periods. This reasoning is even more relevant to thermo-compression plants because here even a little crust formation on the heater leads to a drop in evaporation capacity. In case of substances which tend to crust formation, supersaturation near the heat exchanger walls should be kept as low as possible. This, in general, leads to large heat exchanger surfaces and consequently to higher investments.

#### Summary

In the effort to conceive energy efficient crystallization plants, even small improvements may lead to large savings. Increasing knowledge about individual steps during crystallization also increases the confidence of the planner and the operator in judging the effects of these on the energy balance. Individual phenomenon, like abrasion, formation of secondary nucleation or crust formation, which are crystallization specific, influence the choice of the process and the plant and therefore also the energy balance of the process. With alternative processes and alternative energy sources - we have knowingly not discussed the more spectacular systems like wind energy or solar energy - it is possible to achieve large savings. The large number of different factors makes it essential that in each individual case a detailed costing calculation must be carried out so that one can produce a product at a minimum of cost. The energy minimum point need not necessarily coincide with this value.

As in all branches of industry and chemical technology it is possible to persistently apply our present day knowledge to crystallization also and achieve large energy savings. In closing permit me to support this statement with the following example:

If only a few percent of the world common salt production would be turned to more energy saving processes (e. g. adding a stage more or by using vacuum cooling crystallization or thermo-compression),

then it would be possible to save around 30 000 t of fuel oil per year. This figure should encourage us to do more in this direction.

#### REFERENCES:

- [1] Nývlt, J., Selecting a Suitable Crystallizer  
in: Industrial Crystallization 78  
E. J. de Jong, S. J. Jancić (editors)  
(North-Holland, Amsterdam, 1979)  
405 - 414
- [2] van Wijk, L. A., Incrustation in Crystallizers  
in: Industrial Crystallization 78  
E. J. de Jong, S. J. Jancić (editors)  
(North-Holland, Amsterdam, 1979)  
553 - 554
- [3] Messing, Th., Hofmann, G.,  
Chem.-Ing.Tech. 52 (1980) Nr. 11,  
870 - 874
- [4] Wöhlk, W., Hofmann, G.,  
Chem.-Ing.-Tech. 52 (1980) Nr. 11,  
898 - 900
- [5] Wöhlk, W., Hofmann, G., Operation  
of a large scale KCl crystallization  
plant  
in: Industrial Crystallization,  
J. W. Mullin (editor), (Plenum  
Press, New York, 1976), 461 - 469
- [6] Rautenbach, R., Henne, K.-H.,  
VDI-Berichte Nr. 383, 1980, 47 - 53