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OPERATION OF A LARGE-SCALE KCl CRYSTALLIZATION PLANT

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INTRODUCTION

The crystallization of potassium chloride from mined sylvinite involves a particular problem resulting from the accompanying component, sodium chloride, in the feed solution. To overcome this problem requires very careful planning and the present example of industrial crystallization is ideally suited to describe the many typical problems and their solutions.

Today, the conditions required from a potassium chloride crystallization plant include high capacities (> 100 t/h KCl) most economical operation by reheating the mother liquor with recuperated heat to 80°C , working periods of three weeks without any incrustations and a product with at least 60 wt% of potassium oxide and a mean crystal size of at least 0.6 mm.

The basic process is determined by the composition of the feed solution. For the chosen example, this is given in Fig.1. A product of the specified quality can only be produced by particular measures taken with a view to the solution-flow and the crystallization process. Such measures must be simple and economic to keep the product marketable.

DESCRIPTION OF THE CRYSTALLIZATION PLANT

The operating diagram of the chosen, seven-stage vacuum cooling crystallization plant is presented in Fig.2. This plant produces 140 t/h of potassium chloride from 1200 t/h of feed solution in two parallel seven-stage units. Each stage consists of a turbulence

19,9 wt.-% Potassium chloride
 15,65 wt.-% Sodium chloride
 1,02 wt.-% Magnesium chloride
 1,71 wt.-% Calcium chloride
 0,1 wt.-% Calcium sulphate
 0,25 wt.-% Potassium bromide
 Rest Water

Temperature of Feed: 102 °C

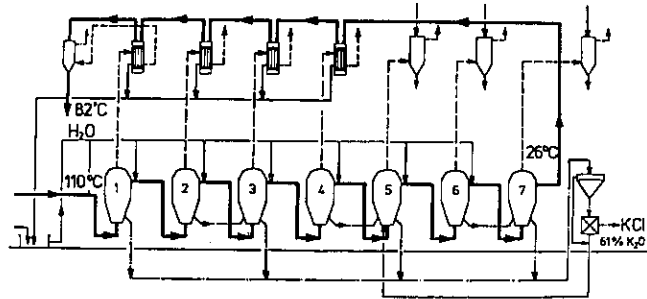


Fig. 1. Raw Solution

Fig. 2. KCl-Crystallisation Plant (2x1670t KCl/d) Operating Diagram

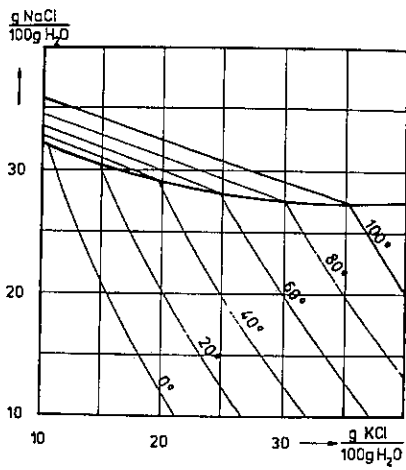


Fig. 3. System KCl—NaCl—H₂O

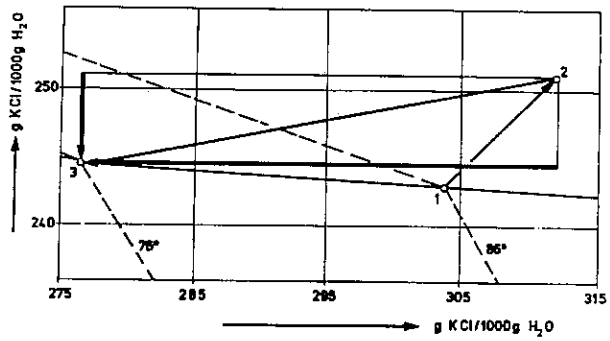


Fig. 4. Crystallisation without Water Addition Vacuum Cooling from 86°C to 76°C

crystallizer. All crystallizers work with the same crystal and suspension residence time, as well as with the same suspension density and supersaturation. The number of crystallization stages resulted from the required reheating of the mother liquor to 80°C and from the final cooling temperature of 26°C which was determined by the available cooling water. Mother liquor reheating is done with the recuperation of heat withdrawn during the preceding vacuum cooling. Of course, only those vapours are used which have a sufficiently high temperature compared with that of the liquor to be reheated. The vapours from the 1st stage, the last heat supplier for the reheating to 80°C , show a temperature of about 74°C . Therefore, indirect heat transfer is not sufficient at this point. As a result of the important boiling point elevation, the required 80°C is finally achieved by condensing vapours direct in the mother liquor. The importance of heat recuperation for the process economy is given by the fact that each additionally recovered degree of heat saves 320000 DM/yr of heating steam costs.

The suspension density of 20 wt% required for the crystallization can only be met on the precondition of providing the separate flow of suspension and mother liquor. This separation of mother liquor and solids is done by the intentionally affected sedimentation in the crystallizers. The overflow of clear liquor from the last crystallization stage is recycled back through the heat recuperation system to the dissolving station. Crystals are withdrawn at four points. This high number of salt discharge points effects an obvious reduction in crystal attrition compared with normal process operation. The suspensions are collected in one prethickener and from there fed into continuously working centrifuges. After separation, the product is dried.

In order to have a long working period free of incrustations, the following factors have been considered: supersaturation only at points where there is sufficient crystal surface available; prevention of heat losses by insulation; prevention of stagnating streams by maintaining permanent flow in all pipes; maintaining the stage temperatures constant by control systems.

The dimensions and arrangements of the erected plant are given on the enclosed photographs. Photograph 1 shows the two parallel, seven-stage units. At the top you can see the three direct contact condensers of the last stages. The photograph was taken at a time when the first set of these two units was already producing. Photographs 2 and 3 allow estimation of the dimensions: they show one of the crystallizers of about 200 m^3 volume.

Process Technique

The process technique is always based on the solubility diagram.

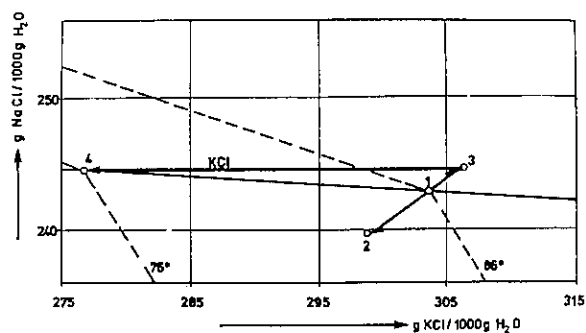


Fig. 5. Crystallisation with Water Addition Vacuum Cooling from 86°C to 76°C

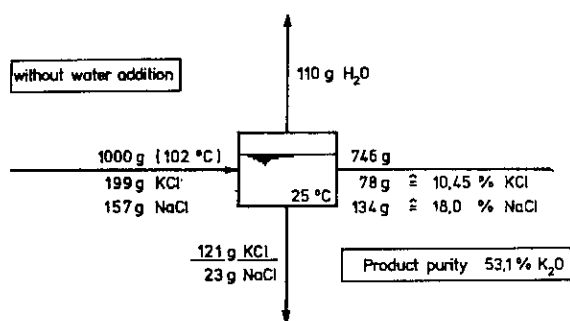


Fig. 6. Product Purity

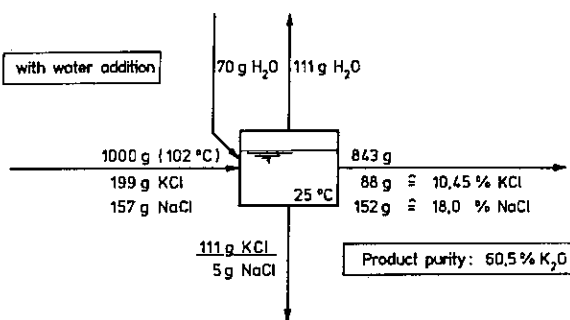


Fig. 7. Product Purity

of the system. In the present case (see Fig.3), potassium chloride, unlike sodium chloride, shows an obvious decrease in solubility by cooling. This explains the choice of vacuum cooling crystallization for the crystallization of potassium chloride from sylvinite. A special feature of this process being used in this system is the necessity of recycling a pre-determined amount of condensate to hinder precipitation of sodium chloride which otherwise is inevitable.

For the second crystallization stage, where the solution is cooled from 86 to 76°C, the concentration relations are given in Fig.4. The solution from the 1st stage has the composition as per point 1. During vacuum cooling, evaporation and cooling happen simultaneously, but for better understanding, the water withdrawal and cooling are shown as two separate operations effected one after the other.

Concentration as per point 2 is reached by evaporation. With regard to the equilibrium temperature of 76°C a supersaturation for both substances, sodium chloride and potassium chloride, results. The supersaturation of sodium chloride, however, has to be hindered because otherwise it would be impossible to obtain the required purity of KCl. This can be done, by adding so much water to the solution from stage 1 to reach point 2 in the solubility diagram (Fig.5). It follows evaporation to point 3 which lies on the horizontal line of point 4. The only resulting supersaturation is that of potassium chloride. Without any water addition, 121 g potassium chloride and 23 g sodium chloride crystallize from 1000 g feed solution. This corresponds to a product purity of only 53.1 wt% (Fig.6).

However, with water addition, every required degree of purity can be achieved. To obtain a product purity of at least 60 wt% potassium oxide, a quantity of added water lower than the quantity of water evaporated by vacuum cooling (Fig.7) will be sufficient.

Among the crystallizers allowing for clear liquor discharge, the classifying and the turbulence crystallizers are the available types. In the present case, the choice between these 2 types was determined, amongst other things, by the investment cost required for equal production capacity. Fig.8 shows a roughly-estimated comparison in size between both types. The classifying crystallizer needs a clearing surface diameter of about 12 to 15 m, while for the magma-type crystallizer a surface diameter of 4.2 m is sufficient. So the type of crystallizer used in this process was that shown in Fig.9. Based on the maximum admissible supersaturation, the internal suspension circulation was determined with 15000 m³/h in each stage. The determination of the largest diameter of 5.4 m resulted from the requirement for a clear liquor overflow.

Parameter	CSCPR	MSMPR
Temp. difference between stages	10 degC	10 degC
ΔT_{max}	1,2 ± 0,8 degC	0,5 degC
Feed	500 m ³ h ⁻¹	500 m ³ h ⁻¹
Circulation	4160 ÷ 6250 m ³ h ⁻¹	10 000 m ³ h ⁻¹
Upstream velocity	10 mm s ⁻¹	10 mm s ⁻¹
Diameter of clarifying surface	12,1 ± 14,9 m	4,2 m
Production	10 t h ⁻¹	10 t h ⁻¹

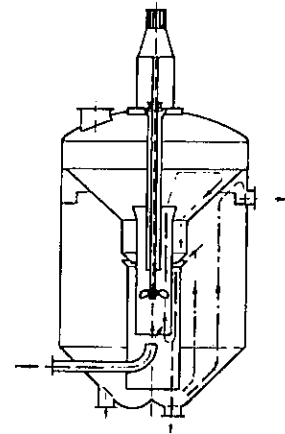


Fig. 8. Comparison of Size: CSCPR/MSMPR for Estimation of Investment

Fig. 9. Standard- Messo Turbulence Crystalliser

98,1 wt.-% Potassium chloride
 ± 62,05 wt.-% Potassium oxide

1,45 wt.-% Sodium chloride
 0,084 wt.-% Calcium chloride
 0,082 wt.-% Magnesium chloride
 0,006 wt.-% Calcium sulphate

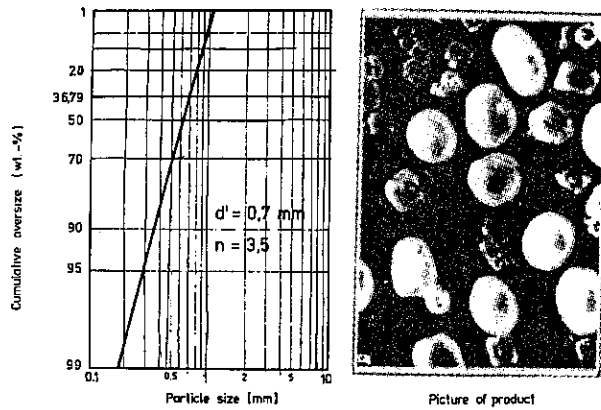


Fig. 10. Analysis - Plant Product

Fig. 11. Product Coming from a Large-Scale KCl-plant

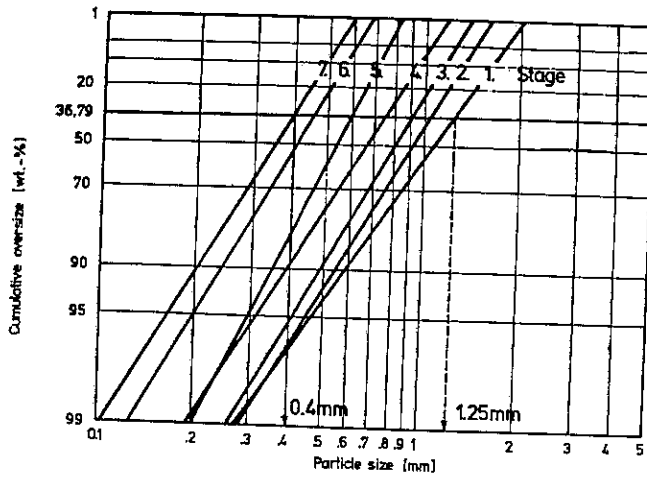


Fig. 12. Crystal Size Distributions in the Stages (RRS).

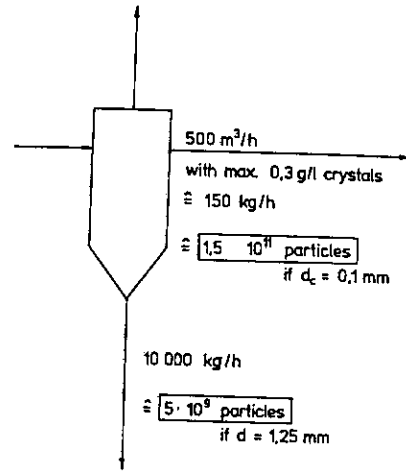
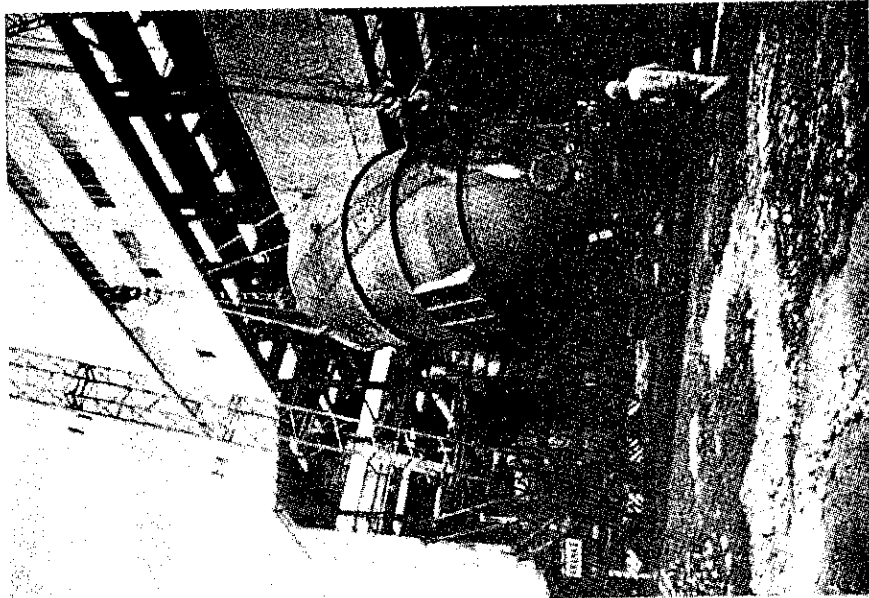


Fig. 13. Calculation of Number of Discharged Particles.



3



2

RESULTS

Due to the imperfection of the parameters, the design of a plant can be evaluated only on the basis of the operating results. The main criteria for such a judgement are, in particular: purity, and crystal size, and also the way of meeting the particular requirements for process engineering such as process technical heat recuperation and long working periods without incrustations.

The above described heat recuperation system provides reheating of the mother liquor to 82°C and thereby exceeds the required value by 2°C. Likewise, the measures which were taken to get a long working period without incrustations proved successful; the working period exceeds three weeks.

The composition of the product obtained from the plant is shown in Fig.10. The product purity of 60 w % potassium oxide is absolutely obtained. It is possible to obtain higher degrees by increasing the amount of added water with reduced production capacity, and vice versa. For a purity reduced to 59 wt% potassium oxide, for example, the capacity of the plant was 130%. Fig.11 shows the crystal size distribution and also a photograph of the plant product.

Parameters Influencing on Crystal Size

The decrease in mean crystal size from 1.25 mm in the 1st stage to 0.4 mm in the 7th stage (Fig.12) is remarkable. However, this is well known in potassium chloride crystallization. Examination showed that one of the reasons was the amount of fines increasing from stage to stage. The number of particles withdrawn in the 'clear liquor' overflow exceeded the number in the removed product by several orders of magnitude, e.g. by 10^2 according to the calculations in Fig.13. In the following stage, these small crystals act as nuclei, and their large number effects a decrease in the mean product crystal size.

As a matter of interest, an analysis was made of those factors which could effect an enlargement of crystal size. The result was that variations in suspension density, residence time and supersaturation appeared to be less important than the dissolution of fines contained in the clear liquor overflow.

Fines dissolution could be made with water added to the system to hinder precipitation of sodium chloride. This would only require the provision of a tank of sufficient volume to meet the time required for dissolution. However, the additional investment cost involved would not justify this possible improvement of the crystal product which was already of marketable quality without that measure.