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Cost effective solution for river water desalinization

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special print from
Chemische Industrie International
XXXVIII/January 1986

Cost effective solution for river water desalinization

This article shows how, in individual instances, measures taken to protect the environment can be combined with the production of re-usable substances so that environmental protection does not only cost money but that its costs can be recovered. Ways of preventing the salinization of our waters is today a topical subject which gives rise to intensive discussions. The potash industry is one of the main culprits responsible for introducing chlorides into rivers, Rhine and Werra being the most notorious examples.

Type and quantity of effluent from the potash industry are determined by the available starting materials, the end products and the different production processes. With conventional production processes three main chloride sources can be distinguished.

- When using the hot dissolution process, sylvinitic salt (potassium chloride with sodium chloride forming the main impurities) is separated into a KCl/NaCl solution for further processing and a solid NaCl residue which is dumped. After the crystallization of potassium chloride the remaining mother liquor, which is almost saturated with NaCl, has to be partly disposed of. The chloride introduced into the rivers stems, in this instance, from dissolved common salt.
- When processing potash salts containing magnesium sulphate the residual solution contains kieserite ($MgSO_4 \cdot H_2O$) and NaCl. Part of this kieserite is converted to potassium sulphate. In order to achieve the required degree of purity a kieserite scrubbing process takes place during which the entire common salt in the residue is dissolved. For each ton of magnesium sulphate up to 4 t of NaCl are discharged with the scrubbing liquor.
- When using carnallitic salts (potassium chloride with magnesium chloride and sodium chloride as main pollutants as well as magnesium sulphate and calcium sulphate) the liquor remaining after potassium chloride crystallization contains a large proportion of $MgCl_2$.

By using alternative processes, which are today used by the potash industry on a large scale, pollution resulting from potassium chloride and potassium sulphate production can be drastically reduced. The main alternative process stages are: Flotation or electrostatic separation (ESTA) of the crude salts and the thermal processing of final liquors. Fig. 1 shows the effects on the water quality of the river Weser (Federal Republic of Germany) resulting from the conversion of all potash production processes in the Werra catchment area to these alternative methods.

The most notable reduction in the load of chloride can be expected from the conversion of kieserite scrubbing, where the electrostatic (ESTA) processes dominate. When using this process the crude salt mixture is passed through an electrostatic field where it is largely split into its individual components. Those components which cannot be further utilised, are deposited in the form of solids.

The processing of final liquors from the KCl production based on carnallitic salts is as effective as is the conversion of hot dissolution processes to the alternatives "Flotation" or "ESTA". The best effects are achieved through the combination of

- Electrostatic separation
- Processing of end liquors containing magnesium chloride.

Economic aspects of final liquor processing

The example of processing a crude carnallitic salt of typical composition – as a simplification Fig. 2 only shows the components KCl and $MgCl_2$ – shows the economic significance of processing the potassium discard solution:

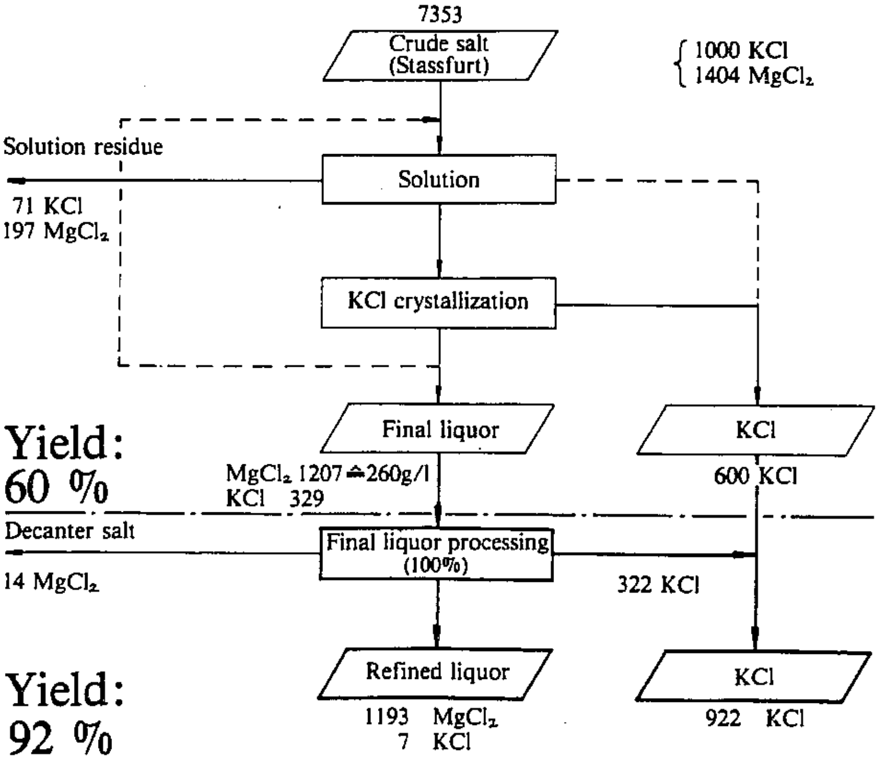
If 100 % processing of the liquor takes place the KCl yield of the process as a whole is increased from 60 to 92 %, and 1.3 t of magnesium chloride in a concentrated purified solution is obtained for each tonne of KCl; the former can either be used directly – for example as regeneration solution for ion exchangers – or processed into magnesium chloride and magnesium oxide.

Fig. 1: Effects of process engineering measures aimed at reducing the salt loads caused by the potash industry.

Measures	*Reduction of chloride load by approx. kg/sCl^-*
1 Flotation for NaCl separation	25
2 Electrostatic separation of NaCl	31
3 Increase in concentration of the final liquors to 75 % by thermal means	39
4 Flotation instead of kieserite washing	83
5 Electrostatic separation instead of kieserite washing	104
Combination of individual measures	
1/4	108
1/3/4	147
2/5	135
2/3/5	174

Problem definition

A potash mine in the German Democratic Republic mines, because the sylvinite deposits are nearing exhaustion, increasing amounts of crude carnallitic salt. When processing the latter into potassium chloride, final liquors are yielded, as described, with magnesium chloride contents of around 260 g/l and other dissolved salts. In order economically to



(Additional components $NaCl_2$, $MgSO_4$ not taken into account)

Fig. 2: KCl production from Stassfurt crude salt with or without final liquor processing

utilise these final liquors and to protect the waterways it was necessary to design a process plant where $MgCl_2$ solutions with the highest possible concentration and the lowest possible amount of impurities can be produced. Specifications are listed in Fig. 3.

Fig. 3: Problem definition: Final liquor processing

	Substance	*% by weight*
From potash final liquor	$MgCl_2$	20.23
	$MgSO_4$	1.95
	KCl	5.53
	NaCl	4.59
To be produced: Refined liquor.	$MgCl_2$	min. 34.07
	$MgSO_4$	max. 1.78
	KCl	max. 0.15
	NaCl	0.44
Decomposition KCl	KCl	min. 56
	NaCl	36
	$MgCl_2$	6.5
	$MgSO_4$	0.5
And to produce as by-products: Mixed salt	Kieserite	41
	KCl	max. 6
	$MgCl_2$	12
	NaCl	41
Water evaporation: Approx. 300,000 tpa		

– Potash discard solution is to be converted to refined liquor

– During this process potassium chloride is to be produced for return into the potash process, with the salt being as pure as is technically and economically justified.

– Accompanying salts from the potash process, which are not wanted in the refined liquor, i.e., in particular magnesium sulphate and sodium chloride must be crystallized out and thus separated from the liquid phase so that they can be easily removed. In order to reduce losses to a minimum the KCl and $MgCl_2$ contents in the salt mixture should be as low as possible.

– The process should be designed so that there is no need to dispose of effluent.

Plant concept

The task of removing from the potash discard solution the substances NaCl, KCl and $MgSO_4$ as well as increasing the concentration of the main constituent $MgCl_2$ takes place in one process, which is dominated by the basic stages evaporation, crystallization, and fractional dissolution. The plant comprises the following main process stages (Fig. 4):

– Cold decomposition of carnallite, which is subsequently crystallized, in a solution that is devised so that $MgCl_2$ is dissolved while the potassium chloride retains its crystalline form.

– Salting out of carnallite from the decomposition liquor by the addition of refined liquor.

– Evaporation of the liquor resulting in crystallization of NaCl and kieserite.

– Cooling of the evaporation liquor resulting in the crystallization of carnallite.

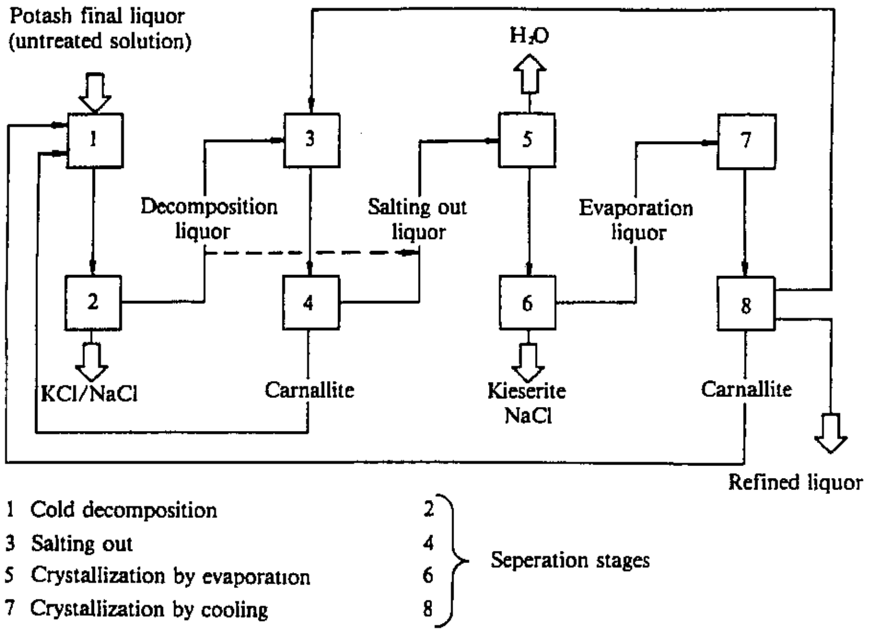


Fig. 4: Basic flow sheet, production of refined liquor

Characteristic points determine solution equilibria

The technological processes taking place within the individual process stages are determined by the solution equilibria.

Fig. 5 shows the characteristic points for the process in the phase diagram KCl-$MgCl_2$-H_2O with NaCl saturation. This diagram is only an approximation of the actual and highly complex solution and does not, for example, take into account that $MgSO_4$ is present in the solution. Nor does the diagram show that others than the listed solids might precipitate.

On the other hand, an awareness of which solids may remain at the bottom of the solution and knowledge of the states of saturation of the other solution components are pre-requisites for a successful process. The development of the most suitable process run and the design of the plant were therefore accompanied by extensive experiments during which all relevant chemical and technical conditions were determined.

The basic concept of the process can be described with the help of Fig. 5: Point A in the diagram marks the input solution into the process, the so-called potash discard solution. To this solution carnallite from subsequent process stages is added. In accordance with the solution equilibrium $MgCl_2$ from the carnallite

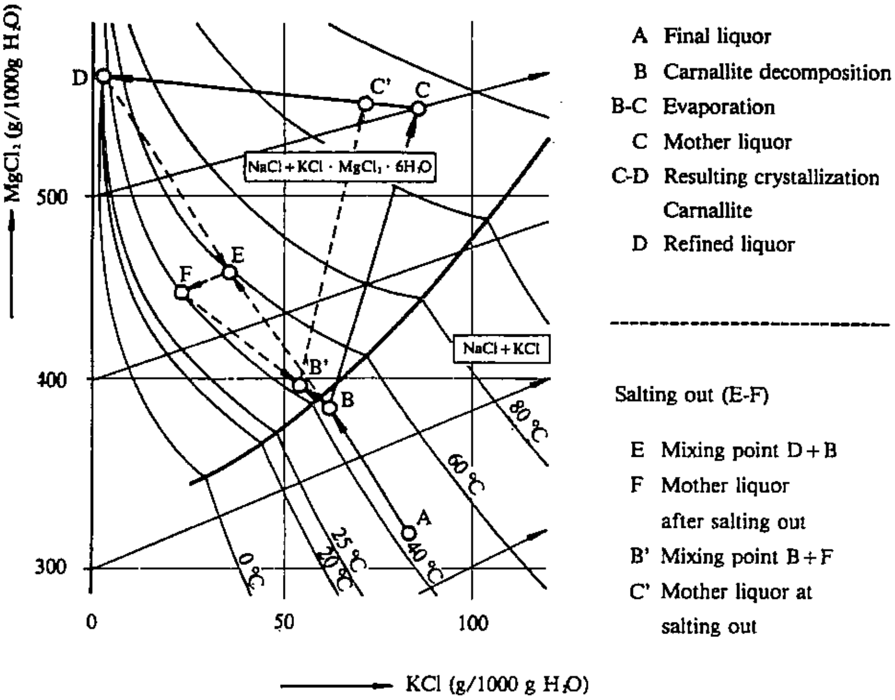


Fig. 5: Process stage for the production of refined liquor from final liquor in the solubility diagram KCl-$MgCl_2H_2O$ (NaCl saturated)

dissolves. KCl crystallizes out while Point B is below the co-existence line KCl/ carnallite in the KCl field.

Crystals that have been separated out are returned to the potash production unit, while mother liquor is evaporated as far as Point C. During the evaporation NaCl and artificial kieserite crystallize out. In order to prevent carnallite crystallization – carnallite precipitation at this stage means KCl and $MgCl_2$ losses – the operating temperature in the evaporation unit must be kept well above the equilibrium temperature of Point C.

Actual processes slightly more complex

After elimination of NaCl and kieserite carnallite is removed from the evaporation liquor in a cooling crystallization unit. During the last cooling stage, which takes place at 25 °C, the required low KCl concentration and simultaneous high $MgCl_2$ content in the refined liquor at Point D is achieved.

Bearing in mind possible fluctuations in the composition of the potash discard solution the actual processes are slightly more complex: the decomposition of carnallite results in a solution, which depending on the concentration of the input solution, has a $KCl/MgCl_2$ ratio of about 0.14 to 0.18. During the evaporation of such solutions there is a tendency of langbeinite $(2\ MgSO_4 \times K_2SO_4)$ rather than the intended kieserite to crystallize out. This leads to undesirable potash losses and insufficient precipitation of magnesium sulphate. Higher $MgSO_4$ concentrations means that the quality of the refined liquor is less good, which means that during cooling crystallization bischofite $(MgCl_2 \times 6H_2O)$ is precipitated before the required $MgCl_2$ concentration has been reached. In order to prevent langbeinite crystallization carnallite salting out means that independent of the process state a $KCl/MgCl_2$ ratio of < 0.14 is attained.

Part of the crystal-free solution (State B), from the decomposition stage is mixed with refined solution of concentration D until the mixing Point E in the carnallite field has been reached. This process is an isothermal one: carnallite crystallizes along the Line E-F. Carnallite is fed into the decomposition unit, crystal-free mother liquor from the salting out stage is mixed with the remaining mother liquor from the decomposition stage so that the input solution for the evaporation plant reaches Point B, where, because of the higher $MgCl_2$ and the lower KCl concentrations, the necessary favourable ratio $KCl/MgCl_2$ of < 0.14 exists.

Practical realisation

The four process stages of

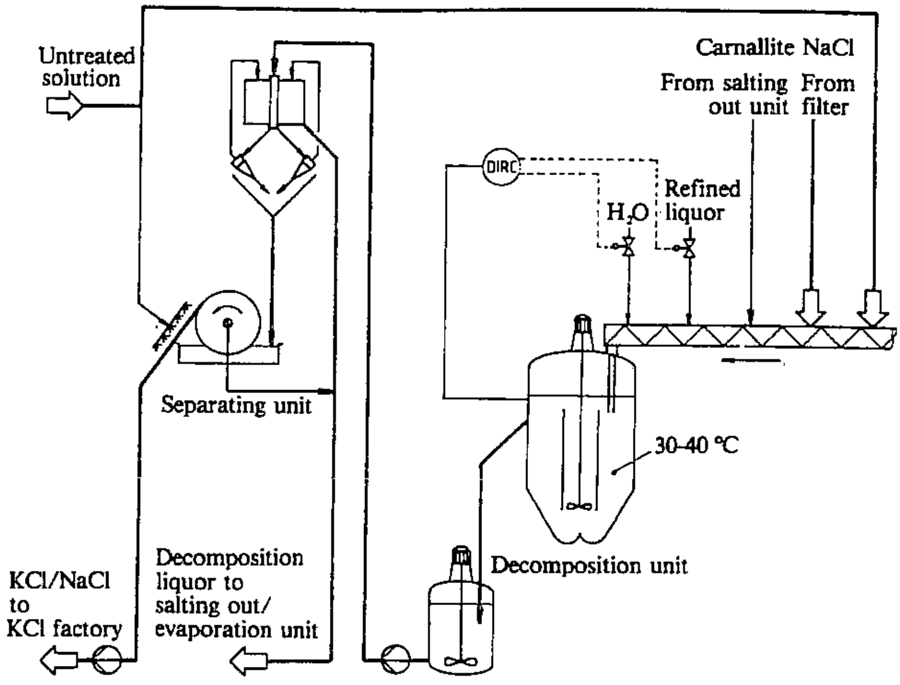


Fig. 6: Carnallite decomposition – schematic diagram

- Carnallite decomposition
- Salting out
- Evaporation
- Carnallite cooling crystallization

were devised on the basis of crystallization-kinetic considerations, so as to keep energy consumption to a minimum, and equipped with measuring and control equipment so that operational efforts are also kept to a minimum.

The decomposition unit (Fig. 6) is a continuously operated shell crystallization unit charged with untreated solution and carnallite as well as with refined liquor or water. Dissolution of $MgCl_2$ and the crystallization of KCl take place simultaneously. KCl formed during this process is returned to the KCl factory, while the crystal-free decomposition liquor is partly conveyed to the salting out unit and partly to the evaporation unit. The carnallite salting out unit (Fig. 7) consists in the main of an agitator crystallizer where, through mixing decomposition liquor and refined liquor carnallite crystallizes out. The suspension, treated in hydrocyclones, is fed into the decomposition unit, while the top product from the hydrocyclone is piped to the receiver of the evaporation unit.

The two-stage counter flow evaporation crystallization unit (Fig. 8) uses forced circulation evaporators. During the hot stage kieserite and NaCl crystal-

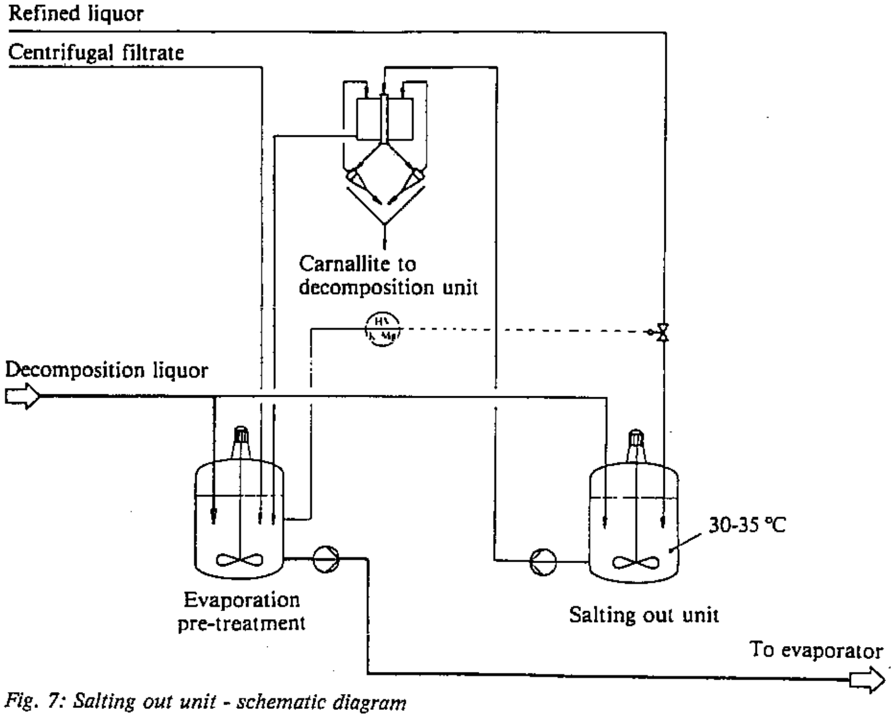


Fig. 7: Salting out unit - schematic diagram

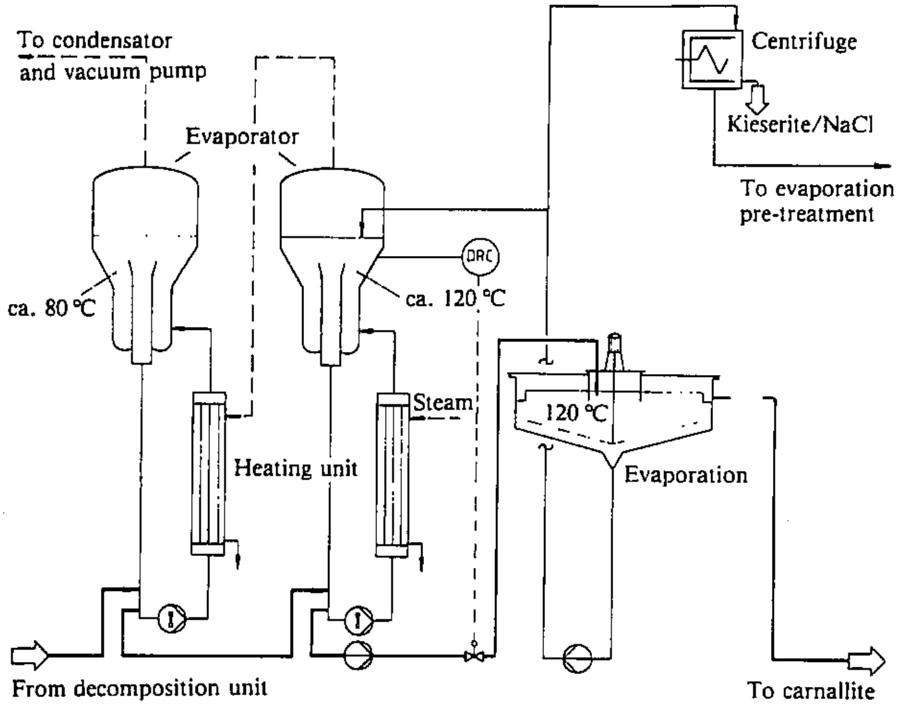


Fig. 8: Evaporator and kieserite separation unit

lize out. The concentration of the suspension is increased in an evaporator, and the solid substances are dumped after separation. The purified overflow of the kieserite evaporator is piped to the carnallite cooling crystallization unit.

The relatively high temperature in this plant section, the corrosive action of the solution and the eroding effect of the suspended kieserite crystals all mean that the materials used must meet special requirements. Depending on the specific location rubber lined or plastic coated materials, Monel and CuA18Fe are being used.

In the four stage carnallite cooling crystallization unit (Fig. 9) the mother liquor is cooled down to about 25 °C. The first two stages take the form of vacuum cooling crystallization units with external circulating pumps while for the last two stages, because of the great increase in boiling points, surface cooling crystallization units were chosen. The crystallized carnallite/NaCl mixture produced during this cooling stage is separated out through evaporators and filters and conveyed to the decomposition unit.

The crystal-free head of the evaporator is taken to the refined liquor storage tanks.

The photograph of the plant model (Fig. 10) gives an impression of the complexity of this process.

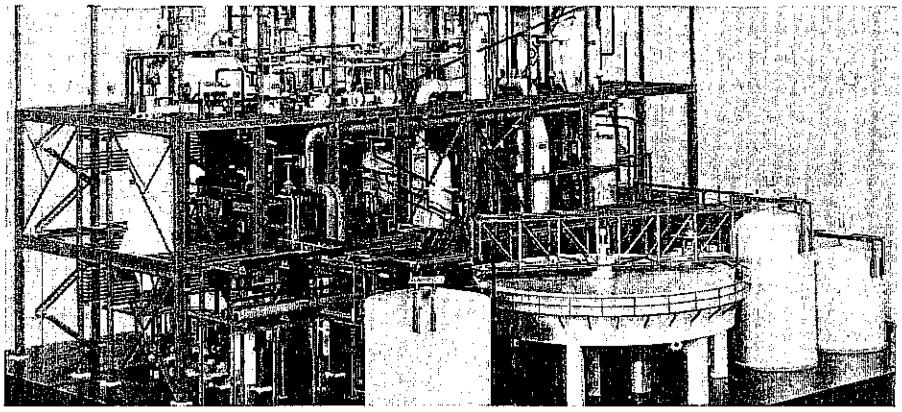


Fig. 10: Model of the plant

Economic utilisation through increased yields and more favourable returns

In the described plant waste liquors from the potash industry are treated so that no effluent occurs. The process thus contributes to reducing the chloride load of the rivers. In addition to this environmental task the plant has a twofold economic advantage:

- The KCl yield of the process is increased.
- The selling price of refined liquor is noticeably higher than its production costs.

As Fig. 11 shows specific production costs amount to DM 74/t, while their sales price is about DM 100/t.

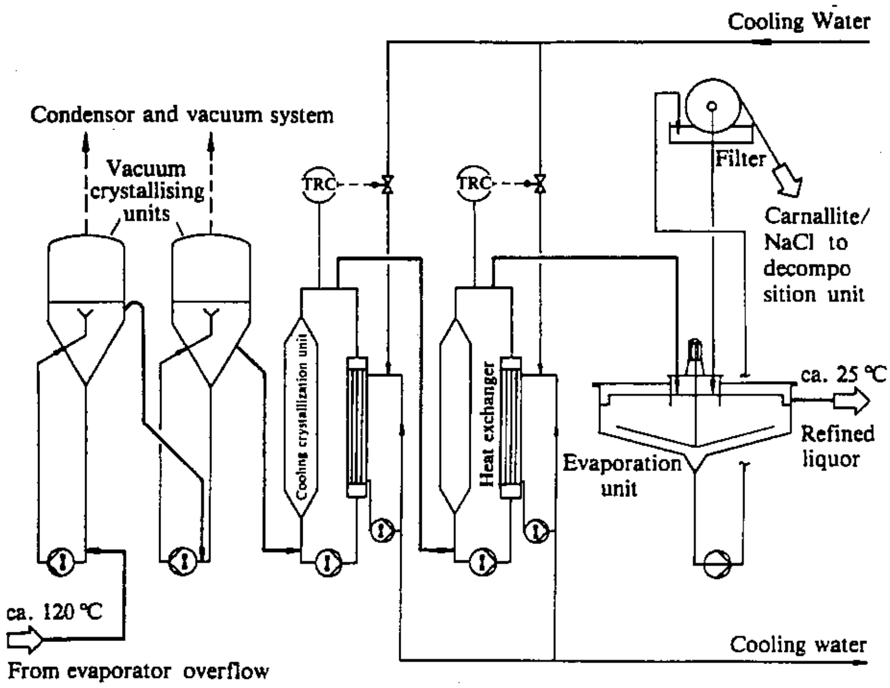


Fig. 9: Schematic diagram of carnallite crystallization

Fig. 11: Specific production costs

Investment Total	*Charge Capital*	*40.00 DM/t*
Heating steam . .	Specific consumption (t/t) 0.4757	
	Charge (at 40 DM/t):	19.03 DM/t
Electricity	Specific consumption (kW/t) 43.49	
	Charge (at 0.12 DM/t):	5.22 DM/t
Cooling water . .	Specific consumption (m^3/t) 27.18	
	Charge (at 0.05 DM/t):	1.36 DM/t
Personnel	Charge:	5.39 DM/t
Maintenance . . .	Charge:	3.00 DM/t
Total costs	Refined liquor	74.00 DM/t