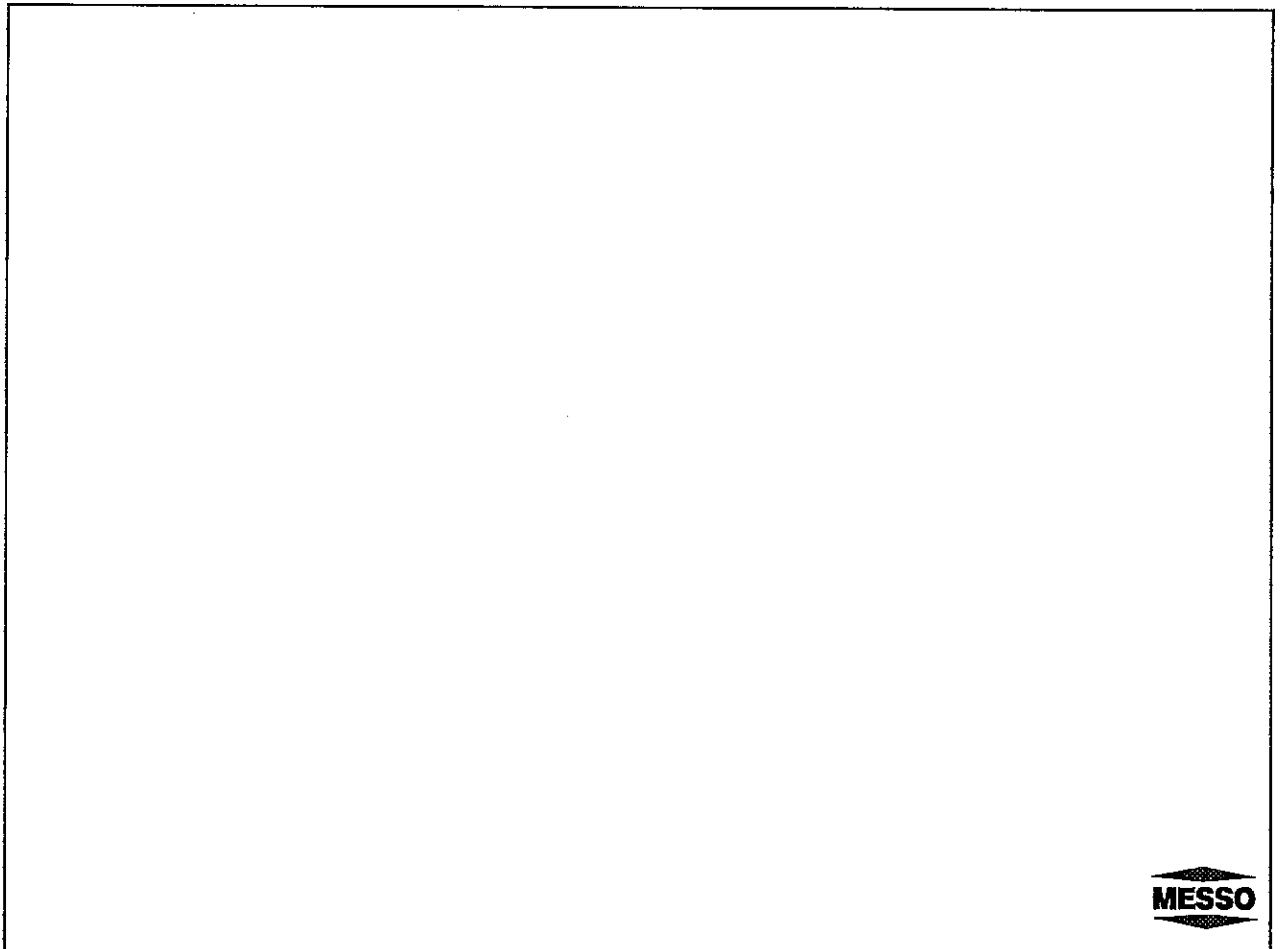


## Potassium Sulphate

### Duisburg's alternative to Mannheim

Heinz Scherzberg, Reiner Schmitz



# Duisburg's alternative to Mannheim

H. Scherzberg, R. Schmitz\*

Messo Chemietechnik has developed a method of producing potassium sulphate by double decomposition of potassium chloride with a magnesium or sodium sulphate under much milder conditions than in the Mannheim kiln. It uses a recirculatory flowsheet to compensate for the inherently incomplete conversion in the reaction.

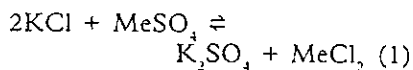
**A**ccounting as it does for only about 5% of the potash fertilizers produced in the world today, potassium sulphate is only of minor importance in quantitative terms. That is no particular surprise because, in contrast to potassium chloride, pure potassium sulphate is very rarely found in nature and in most cases has to be produced by chemical reactions.<sup>1,2</sup> But, even though it costs twice as much, potassium sulphate has a number of advantages which justify its application under such circumstances that demand for it may be expected to increase further<sup>3,4</sup>.

There are three main advantages to potassium sulphate as a fertilizer. First, in addition to its potassium content (50-53% K<sub>2</sub>O), it also contains some 18% sulphur, itself an essential plant nutrient. Second, it has both a low salt index, so does not contribute significantly to soil salinization, and a low chloride content, making it suitable for chloride-sensitive crops. Third,

it gives a higher crop yield than potassium chloride.

## Possible production routes

The raw material for potassium sulphate production is potassium chloride, which is converted by double decomposition with a sulphate component in a single- or multi-stage process according to the equation:



The component supplying the sulphate governs the position of the equilibrium and hence the primary yield of the conversion reaction. The following materials are contenders for use as the sulphate supplier.

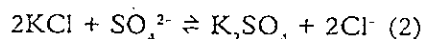
- sulphuric acid
- magnesium sulphate and its hydrates
- sodium sulphate and its hydrates
- calcium sulphate and its hydrates

Even today, a large proportion of potassium sulphate is produced with sulphuric acid at high tempera-

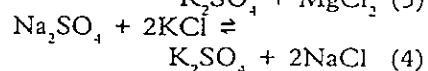
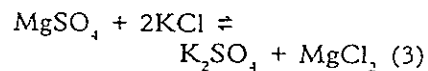
tures according to the Mannheim furnace process. However, because hydrogen chloride is formed simultaneously that process needs an outlet for hydrochloric acid, preferably in the immediate vicinity, and that considerably limits its applicability. When using calcium sulphate no effective yield is obtained in aqueous solutions so that, apart from the exceptional position of sulphuric acid, magnesium and sodium sulphates remain the main sulphate carriers.

## Fundamentals of process management

General conversion takes place in a system of reciprocal salt pairs in aqueous solution according to the equation



Such salt pairs are

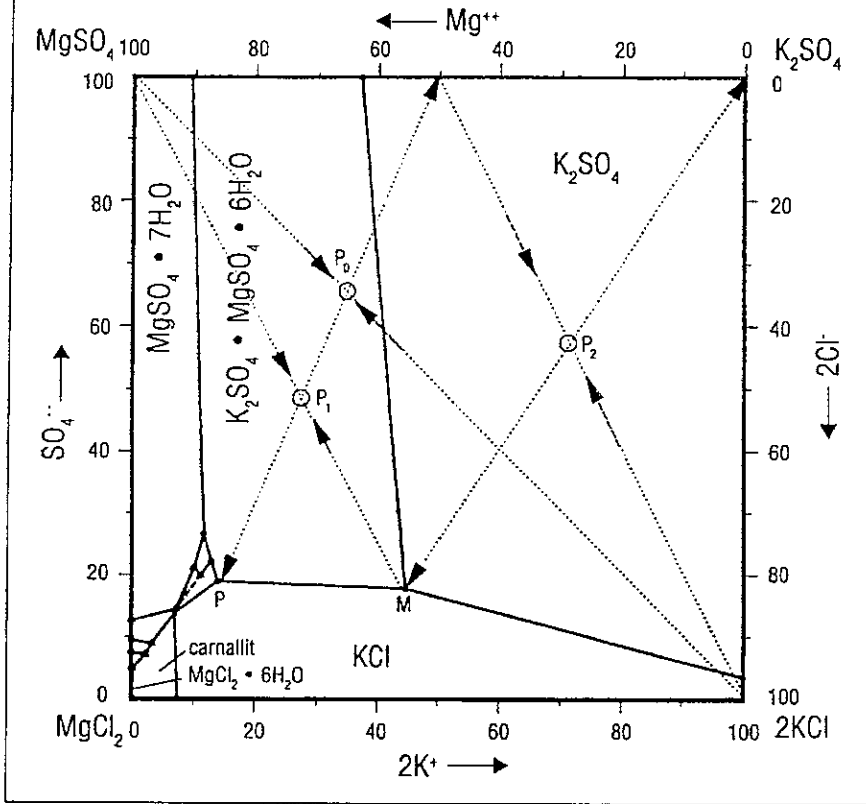


Potassium sulphate is obtained as a sparingly soluble salt at a yield

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Fig. 1: Equilibrium Diagram for the System  $2\text{KCl} + \text{MgSO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MgCl}_2$  at 25 °C



which varies as a function of the temperature and the nature of the other cation but is incomplete in any case. In addition to the target product potassium sulphate, the double decomposition results in a supernatant liquor which contains considerable amounts of the starting materials as well as the chloride compound resulting from the reaction. Above all, the solubility equilibrium governs the practicability, problems and complexity of the process management.

Figures 1 and 2 show the equilibria of the reciprocal salt pairs when using  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$  respectively in the Janicke diagram. It can be seen that in both systems, the final product potassium sulphate has no line of coexistence in common with the respective by-product  $\text{MgCl}_2$  (aq) or  $\text{NaCl}$ , so that potassium sulphate double-salts ( $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4$  (aq) or  $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ) must first be produced in such a process; from these double salts, potassium sulphate is subsequently obtained by decomposition. Even then, the yield of both potassium and sulphate is incomplete because the process solutions which must be withdrawn from the process still contain dissolved potassium and sulphate ions.

That potassium sulphate can be produced at low cost at all on the basis of double decomposition with sulphates other than sulphuric acid is primarily due to the fact that these potassium processes are not run separately but are integrated into an overall potash ore processing scheme in which the incomplete conversion is mitigated: potassium chloride recovery in the potassium chloride production stage largely compensates for the incomplete potassium yield in the potassium sulphate stage. In Germany, for example, where potassium chloride and magnesium sulphate occur in the same evaporite series, the potassium sulphate process can be an integral part of the surface facilities at the mine. That is not a possibility where the potassium sulphate is produced at a location remote from the potassium chloride winning site, as, for example, at a natural sulphate source like a salt lake. If potassium chloride must be purchased, the potassium yields of 60-

Fig. 2: Equilibrium Diagram for the System  $2\text{KCl} + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + 2\text{NaCl}$  at 25 °C

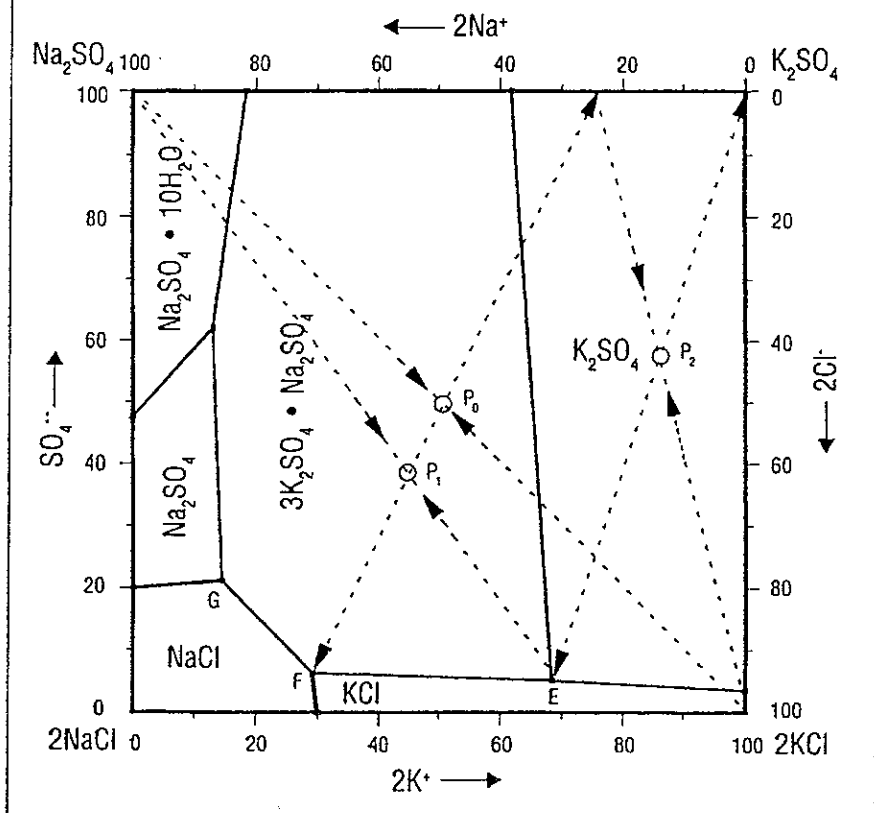
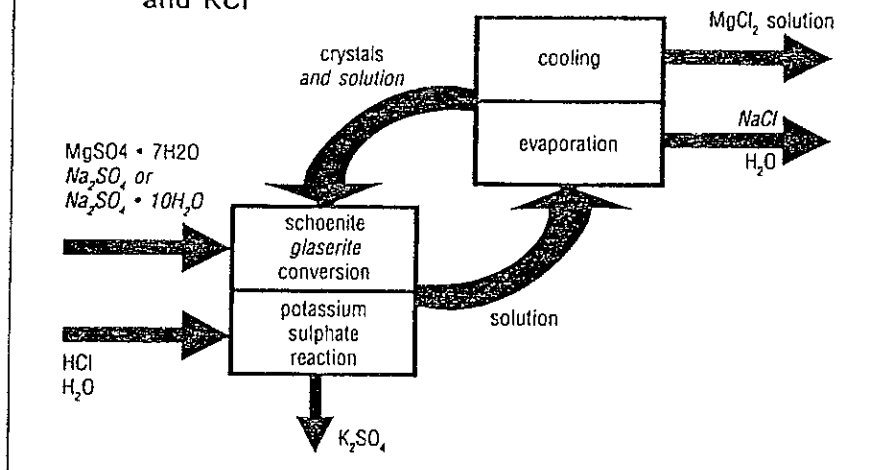


Fig. 3: Cyclic Process for  $K_2SO_4$  from  $MgSO_4$  or  $Na_2SO_4$  and KCl



65% typical for the process are unacceptable from the economic point of view, even if the sulphate component is available practically free of charge.

## Cyclic potassium sulphate processes

The way out of this difficulty is to use a cyclic process in which the raw materials required for potassium sulphate production are fed in stoichiometric quantities and the unconverted raw material components remaining after crystallization and separation of the potassium sulphate are recovered. The internal structure of such a cycle is dependent on the nature of the raw material component containing the sulphate.

Figure 3 illustrates in simplified form a cyclic process for producing potassium sulphate from potassium chloride and either "bitter salt" (Epsom salt),  $MgSO_4 \cdot 7H_2O$ , or alternatively anhydrous sodium sulphate ( $Na_2SO_4$ ) or Glauber's salt ( $Na_2SO_4 \cdot 10H_2O$ ).

By adding magnesium or sodium sulphate in solid form to a high-concentration potassium chloride solution, the double salts schoenite ( $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ ) or glaserite ( $3K_2SO_4 \cdot Na_2SO_4$ ) are formed in the first conversion stage and then converted to potassium sulphate by reaction with KCl only in a second process stage. The water required for solution equilibria must be evaporated and is partly discharged as an  $MgCl_2$  solution. All in all, a closed cycle process results

from which only the target product potassium sulphate, the added process water and the respective by-product sodium chloride in solid form or magnesium chloride as a concentrated solution are discharged from the process at various points.<sup>6,7</sup>

In each instance, the basic process principle is illustrated in the equilibrium diagrams:

The double salt glaserite or schoenite and the solution F or P are obtained in the first conversion stage by converting the sulphate component with a solution E or M if the masses fed correspond to the mixing point  $P_1$ . After separation of this intermediate product, the double salt is converted with KCl

solution to potassium sulphate and the solution E or M at the mixing point  $P_2$  in the second stage. The solution E (M) is recirculated to the first stage. The addition of the dissolving water required in the second stage must be compensated by evaporation at a suitable point in the process.

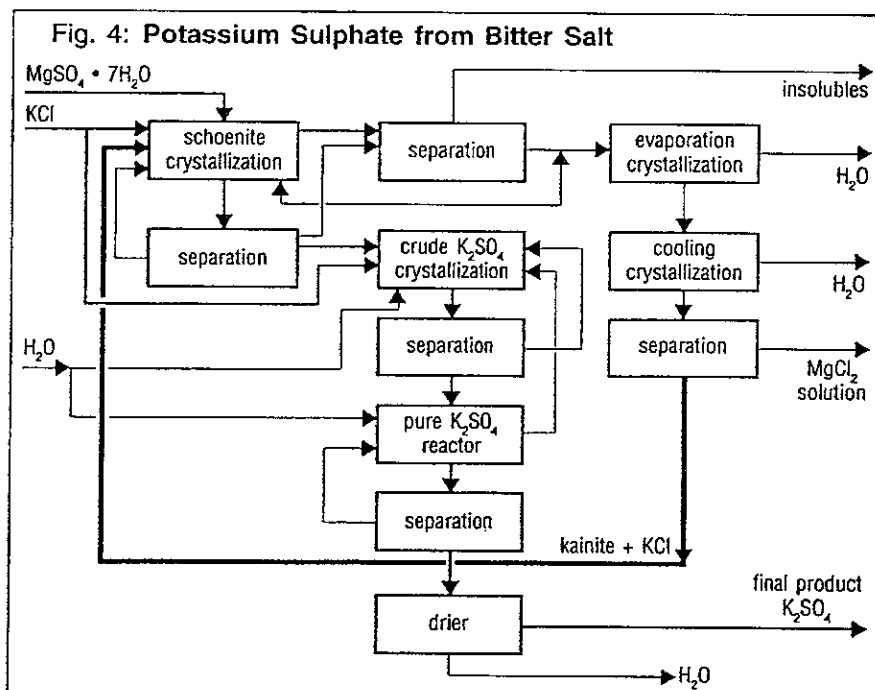
Although the equilibrium diagrams appear to be similar at first sight, the two processes differ considerably. For instance, if magnesium sulphate is used, a concentrated  $MgCl_2$  solution is obtained at best, whereas when sodium sulphate is used solid NaCl is produced and therefore the process gives rise to no liquid residual substances.

## Production from magnesium sulphate

In the potash industry, Epsom salt is customarily the most important sulphate-supplying raw material for potassium sulphate production. It is obtained from kieserite ( $MgSO_4 \cdot H_2O$ ), which itself is a constituent of the crude salts of the Zechstein deposit in Central Germany.

If Epsom salt or magnesium sulphate hexahydrate ( $MgSO_4 \cdot 6H_2O$ ) is available from natural sources of brines or salt lakes as a basic raw material and potassium sulphate is to be produced inde-

Fig. 4: Potassium Sulphate from Bitter Salt



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pendent of a potash production process, the basic operations required are similar to those of the potash industry's classical potassium sulphate process<sup>8</sup>. Figure 4 shows a process flow diagram including an evaporation stage. The process illustrated here was especially developed for locations at which  $K_2SO_4$  production is performed separately from other potash processes. As a result, the yield can be increased to >90 % for the introduced potassium and 92% for the introduced sulphate.

1.6 m<sup>3</sup>  $MgCl_2$  solution containing 0.5 tonne  $MgCl_2$  arise per tonne of potassium sulphate.

This cyclic process commences with a first reaction stage in which the bitter salt is converted to the double salt schoenite ( $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ ) at ambient temperature with potassium chloride solution and the crystals from the evaporation stage. Potassium sulphate production from schoenite corresponds to the process operation used in the German potash industry. All the dissolving water required for the reaction is introduced into this process stage. Magnesium chloride formed in this stage remains in the liquid phase and has to be discharged from the circuit at a rate balancing the water added to the circuit in the form of water of crys-

tallization and process water.

Both operations are performed by evaporating the supernatant liquors up to the highest possible magnesium chloride concentration. Water is evaporated in modern forced-circulation evaporative crystallizers with external heaters. Multi-stage designs reduce the specific steam requirement<sup>9</sup>. This procedure serves not only to adjust the water balance in the circuit but also to promote crystallization of potassium chloride and magnesium sulphate as a potassium chloride-kainite mixture ( $KCl + KCl \cdot MgSO_4 \cdot 3H_2O$ ). This is reintroduced into the cycle after cooling and separation. Magnesium chloride is bled from the circuit as a concentrated solution (300-320 g/l) at a rate corresponding to the amount of potassium sulphate formed.

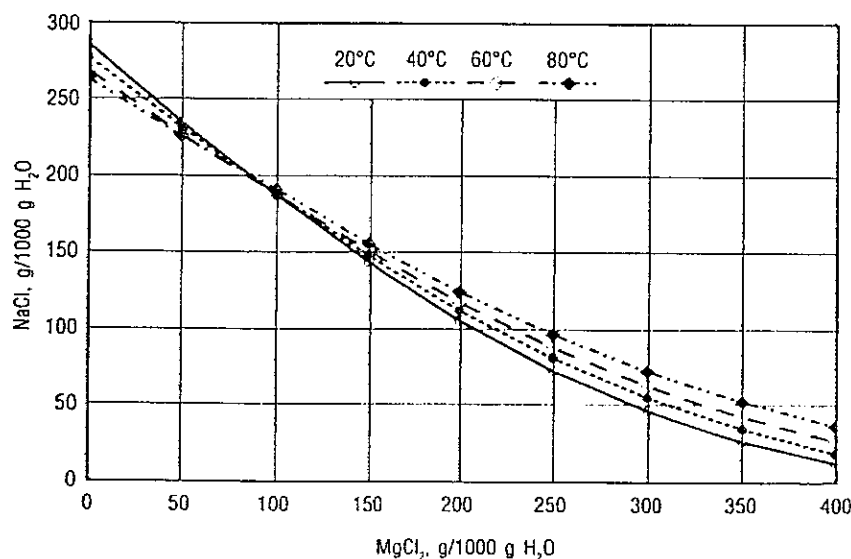
The sodium introduced with the raw materials is of special significance. Because of the limited solubility of sodium salts in magnesium chloride solutions, either low-sodium raw materials must be used or the raw materials must be treated in an upstream process stage to reduce their sodium content. The amount of sodium introduced has a critical effect on the yield and the achievable magnesium chloride concentration, as can be seen from Fig. 5.

## Production from sodium sulphate

Another very common sulphate raw material is Glauber's salt (sodium sulphate decahydrate), which is found in natural deposits, obtained in processes involving the cooling of brines, or produced as a waste product of certain industrial processes. A process permitting immediate utilization for potassium sulphate production has been developed as an alternative to the usual calcination to water-free sodium sulphate. As can be seen from Fig. 2,  $K_2SO_4$  and  $NaCl$  have no line of coexistence in common. That means that, as in the case of the magnesium sulphate system, a potassium sulphate process based on Glauber's salt or sodium sulphate must likewise have at least two reaction stages, in which the double salt (in this case glaserite,  $3K_2SO_4 \cdot Na_2SO_4$ ) is first formed and then decomposed in a thermal evaporation stage, where the process water and the crystallization water introduced are extracted and sodium chloride is crystallized in solid form.

Figure 6 illustrates this cyclic process schematically for the case in which anhydrous sodium sulphate is used. In a further development of an earlier concept,<sup>6,7</sup> the  $NaCl$ -containing glaserite mother liquor resulting from the conversion is fed directly into the evaporation stage without intercooling; even so, pure  $NaCl$  is crystallized.<sup>10,11</sup> That is quite possible when the glaserite mother liquor has a solution composition which is close to the point at which glaserite,  $NaCl$  and  $KCl$  can all coexist. In such a case, potassium yield in the conversion itself is at its lowest but  $SO_4^{2-}$  concentration in the mother liquor is also near the theoretical minimum. But, in fact, these partial yields are unimportant for the continuous process. The glaserite mother liquor can be evaporated to crystallize  $NaCl$  without sulphate separation. Figure 7 illustrates the position of the straight line of evaporation in the solubility diagram. Pure sulphate-free common salt for use as industrial or table salt can be produced in this manner. If Glauber's salt is used in place of

Fig. 5:  $NaCl$  Saturation as a Function of  $MgCl_2$  Concentration in System  $NaCl - KCl - MgCl_2 - MgSO_4 - H_2O$  ( $KCl$  saturation, 40g  $MgSO_4/1,000g H_2O$ , 20-80°C)



anhydrous sodium sulphate, the crystallization water introduced must be evaporated in another evaporation stage. It depends on local conditions whether it is more advantageous to first produce anhydrous sodium sulphate from Glauber's salt or to use the Glauber's salt directly and evaporate the crystallization water in the cycle described.

## Potassium sulphate or double salts as target product

When planning a process for producing chloride-free sulphatic potash fertilizers the question has to be answered whether it is absolutely necessary to invest in the high technology and expend the energy needed to convert the double salt obtained to potassium sulphate or whether it is not more practical to dry the double salt and discharge it from the process as a product in its own right. This is applicable in

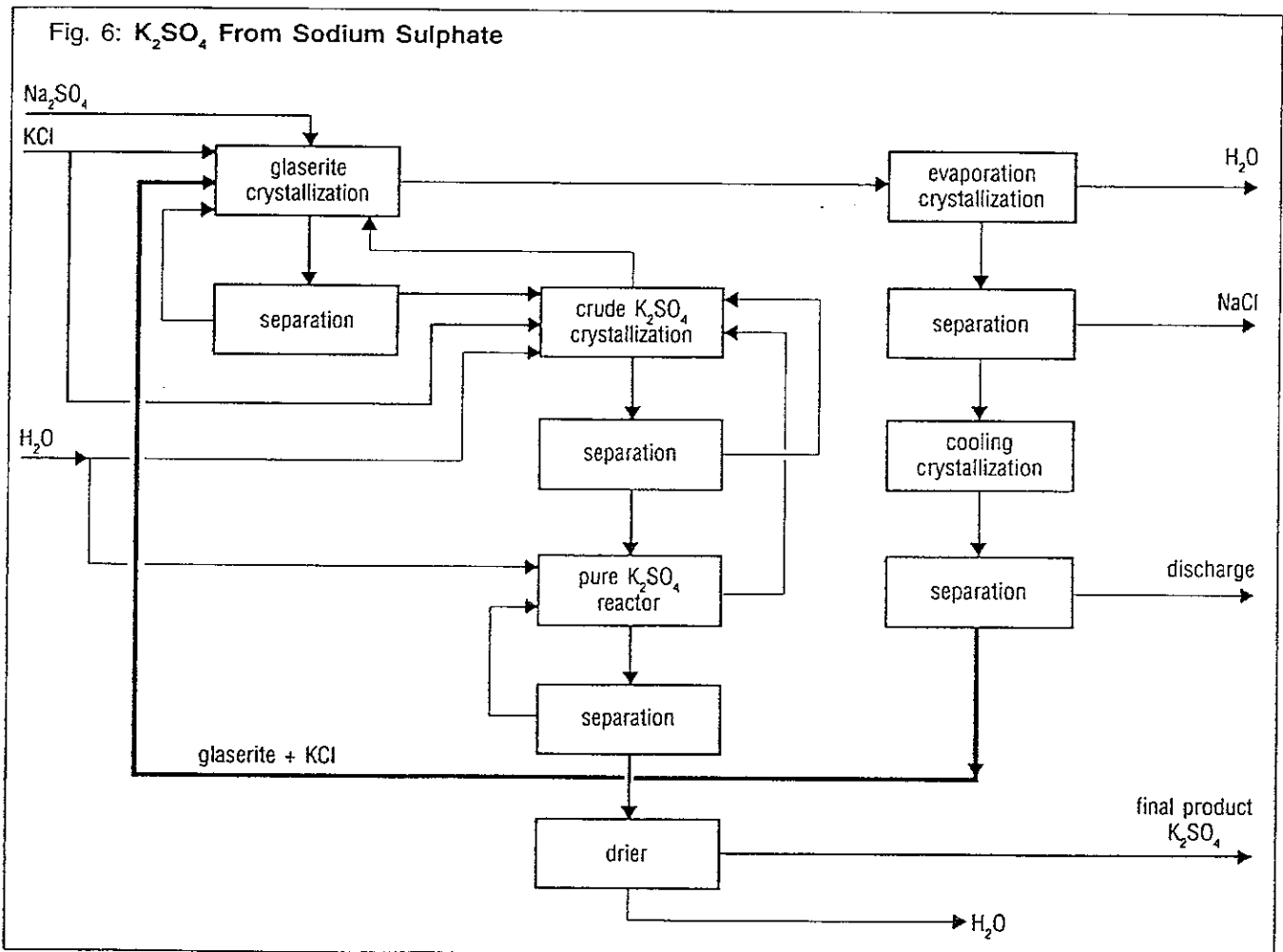
particular to that process line in which sodium sulphate is used as a sulphate carrier. Although schoenite can be calcined to a potassium-magnesium fertilizer with 30%  $K_2O$  and 13%  $MgO$  and granulated, the expenditure on evaporation of the crystallization water (as much as 1 tonne  $H_2O$ /tonne  $K_2O$ ) is very high. Glaserite contains about 40%  $K_2O$  and can, in principle, be used like potassium sulphate as a fertilizer for plants sensitive to chloride. Glaserite as final product in a cycle considerably reduces the expenditure in terms of process technology and energy: from the initial separation stage in Fig. 6, the product passes directly to the drier, and the rest of the middle bank of process stages (crude  $K_2SO_4$  crystallization, separation, pure  $K_2SO_4$  reactor, separation) and their associated  $KCl$  and  $H_2O$  feeds are omitted.

Glauber's salt, potassium chloride and recycled suspension from the evaporative crystallizer are converted to glaserite in a single stage.

The glaserite is separated and dried and represents the saleable chloride-free fertilizer containing 40%  $K_2O$ . The glaserite mother liquor is evaporated and  $NaCl$  is crystallized in an amount corresponding to that produced by glaserite formation in the cycle. Because conversion of glaserite to potassium sulphate is dispensed with, all the water that would have been required for that stage is not needed either, so that only the crystallization water of the Glauber's salt and the additional water required for maintaining the dissolution of the  $NaCl$  formed by the reaction have to be evaporated.

The advantages and disadvantages can be seen from the comparison of the respective characteristic data in Table I. In each instance, the characteristic data relate to 1 tonne  $K_2O$  in the product.

The production of a  $K-Mg-SO_4$  fertilizer does not provide any process technological advantages as compared to potassium sulphate production because the high pro-



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**Table 1**  
Consumptions and Yields of Various Process Options

Final product	K <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	Glaserite	K <sub>2</sub> SO <sub>4</sub>
Raw material	Na <sub>2</sub> SO <sub>4</sub>	Glauber salt	Glauber salt	Epsom salt
<i>Specific consumption</i>				
KCl (60% K <sub>2</sub> O) †	1.7	1.7	1.7	1.85
Na <sub>2</sub> SO <sub>4</sub> †	1.6	-	-	-
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O †	-	3.6	5.0	-
MgSO <sub>4</sub> ·7H <sub>2</sub> O †	-	-	-	2.8
<i>By-product</i>				
NaCl †	1.2	1.2	1.2	-
MgCl <sub>2</sub> solution m <sup>3</sup>	-	-	-	3.2
† MgCl <sub>2</sub>	-	-	-	1.0
<i>Evaporation</i>				
† H <sub>2</sub> O	4.5	6.5	4.5	2.3
<i>Final product</i>				
† product	2.0	2.0	2.5	2.0
† K <sub>2</sub> O	1.0	1.0	1.0	1.0
% K <sub>2</sub> O	50-53	50-53	40	50-53
% Na <sub>2</sub> SO <sub>4</sub>	6-1	6-1	25	-
<i>Yield</i>				
% K <sub>2</sub> O	>96	>96	>96	>90
% SO <sub>4</sub>	>98	>98	>98	>92

portion of water of crystallization has to be removed in the drying section. In contrast to this, the production of glaserite as final product instead of potassium sulphate is of advantage in particular when Glauber's salt is available.

## Solar energy for water evaporation

Wherever it can be utilized, solar energy is the cheapest form of energy for evaporating water. In those salt zones with brines and sulphatic mineral deposits located in the arid climatic zones a conversion process using solar energy<sup>12</sup> is

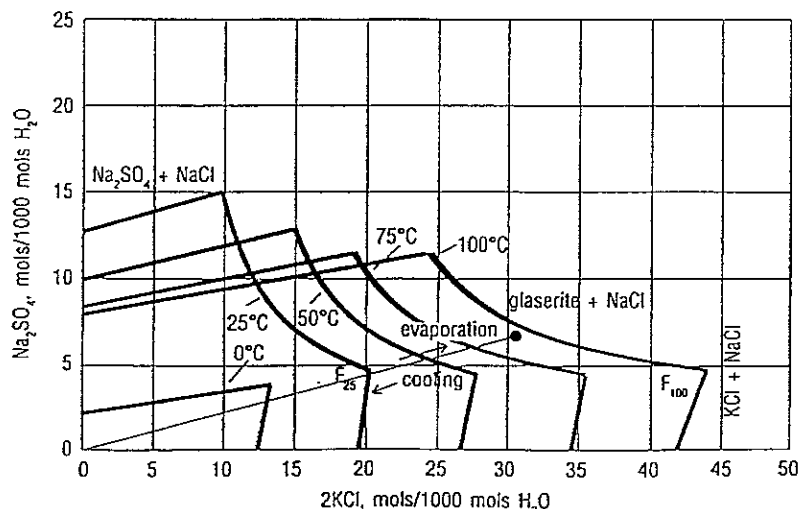
virtually mandatory. Besides the conversion stages, a cycle for converting Glauber's salt or Na<sub>2</sub>SO<sub>4</sub> into glaserite requires a separate solar pond, in which the water evaporates and the sodium chloride crystallizes. Because both the conversion and the solar evaporation work at almost the same temperature, NaCl can be crystallized as a pure sulphate-free product only if the SO<sub>4</sub> concentration in the glaserite mother liquor is reduced by prior cooling to a temperature around 0°C to promote crystallization of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, which is recycled to the initial glaserite crystallization stage. Pure sodium chlo-

ride can then be obtained by solar evaporation from the solution separated from the crystallized Glauber's salt until either SO<sub>4</sub><sup>2-</sup> or KCl reaches its saturation point. The brine from the solar pond is recycled into the glaserite crystallization stage. ■

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Fig. 7: Glaserite Mother Liquor Crystallization Regime



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