

# Messo pilots new potassium sulphate process

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Messo-Chemietechnik has successfully completed pilot trials on a new process for converting sodium sulphate and potassium chloride to glaserite and then to potassium sulphate and usable sodium chloride in continuous crystallizers. The process can accept by-product Glauber's salt and waste potash brines in place of high-grade raw materials.

**P**otassium sulphate ( $K_2SO_4$ ), with a  $K_2O$  content of 54.06%, is slightly inferior as a source of plant nutrient potash to potassium chloride ( $KCl$ ), which has a  $K_2O$  content of 63.18%. But it has a very definite advantage in that its anionic portion is sulphate, which is more favourable for plant physiology than the substantial chloride content (47.55%) of potassium chloride. Potassium sulphate has, in fact, become the most important chloride-free potash fertilizer and holds a steady place in the product range of potash fertilizers, even though it is twice as expensive per tonne of  $K_2O$  as potassium chloride. Indeed, demand for this high-grade fertilizer is increasing.

Potassium sulphate occurs naturally only seldom in a pure state. But it is found in some potash deposits in the form of double salts, for example langbeinite, from which it can be recovered by multiple-stage processes.

In principle, however, it is also possible to produce potassium sulphate from potassium chloride by double conversion with a sulphate-containing raw material such as sulphuric acid, magnesium sulphate, calcium sulphate, sodium sulphate and ammonium sulphate. Table I shows the respective reaction equations and the nature and quantity of the secondary product that is automatically recovered per tonne of potassium sulphate.

## Factors affecting process choice

An important consideration is the utility of the by-product, and in that respect the most favourable option is to produce potassium sulphate from sodium sulphate. The recovered sodium chloride may be used as industrial or table salt. All other reaction paths result in the recovery of by-products that will either necessitate further processing (like hydrogen chloride) or cause major environmental problems when discharged into the drainage system (like magnesium or calcium chlorides)<sup>3</sup>. From the point of view of environmental protection, the only circumstance under which it

**Table I**  
Basic Reaction Paths for Production of Potassium Sulphate from Potassium Chloride

Sulphate raw material	Reaction equation	By-product	
		Compound	Theoretical amount (t/t $K_2SO_4$ )
$H_2SO_4$	$2KCl + H_2SO_4 \rightleftharpoons K_2SO_4 + 2HCl$	HCl	0.418
$MgSO_4$	$2KCl + MgSO_4 \rightleftharpoons K_2SO_4 + MgCl_2$	$MgCl_2$	0.546
$CaSO_4$	$2KCl + CaSO_4 \rightleftharpoons K_2SO_4 + CaCl_2$	$CaCl_2$	0.637
$Na_2SO_4$	$2KCl + Na_2SO_4 \rightleftharpoons K_2SO_4 + 2NaCl$	NaCl	0.671
$(NH_4)_2SO_4$	$2KCl + (NH_4)_2SO_4 \rightleftharpoons K_2SO_4 + 2NH_4Cl$	$NH_4Cl$	0.614

might conceivably be justifiable to discharge the latter kind of effluent is if the plant is located in a coastal area.

Although, in principle, it might seem favourable to use calcium sulphate as the sulphate carrier, the problems involved in translating the corresponding process concepts into a practical embodiment are virtually insurmountable: the solubility of calcium sulphate is so low and the position of the equilibrium so far on the side of the raw materials that complicated processes are required.

There is another factor in favour of using sodium sulphate: sodium sulphate solutions are generated as by-products in several industrial processes, among which flue gas desulphurization should be mentioned. These solutions have to be processed for environmental reasons.

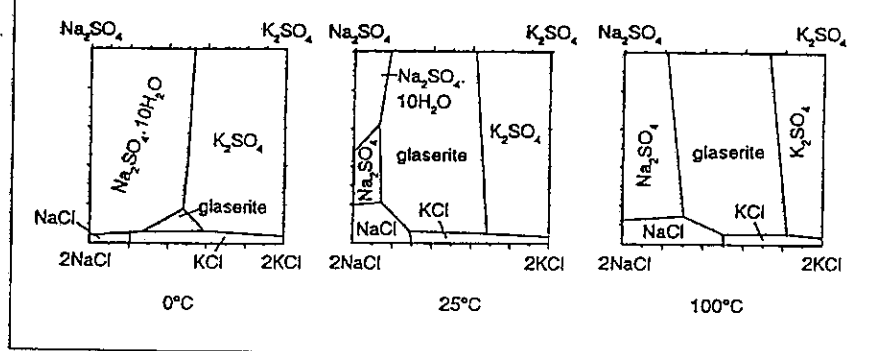
The traditional production processes for potassium sulphate from potassium chloride are based either on conversion with sulphuric acid, according to the Mannheim furnace process, or on double decomposition with magnesium sulphate. Hitherto conversion of sodium sulphate to potassium sulphate – which is more favourable in terms of both economics and ecology – has been used in only a few cases. In Soligorsk, Belorussia, there is an industrial potassium sulphate production plant working on the basis of sodium sulphate, but the by-product sodium chloride is produced only as a liquid effluent.<sup>4, 5</sup>

## Theory of $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ conversion

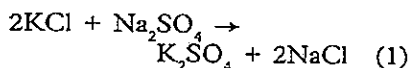
The conversion of potassium chloride with sodium sulphate in aqueous solution is governed by the solution equilibria of the potentially participating and formed salts  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and the double salt glaserite ( $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ ) in aqueous solution.

Figure 1 presents phase diagrams for the system  $\text{KCl}$ - $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ - $\text{NaCl}$  at various temperatures.<sup>6</sup> The areas which define the concentration ranges in which

Fig. 1: Solution Phase Diagrams for the Aqueous  $\text{Na}^+/\text{K}^+/\text{Cl}^-/\text{SO}_4^{2-}$  System at 0°, 25° and 100°C

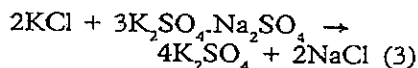
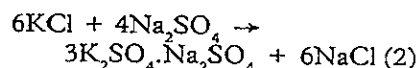


potassium sulphate and sodium chloride can exist do not adjoin one another at any temperature; consequently, it is not possible in a single process step to transform potassium chloride and sodium sulphate into potassium sulphate and sodium chloride in the manner shown in equation (1).



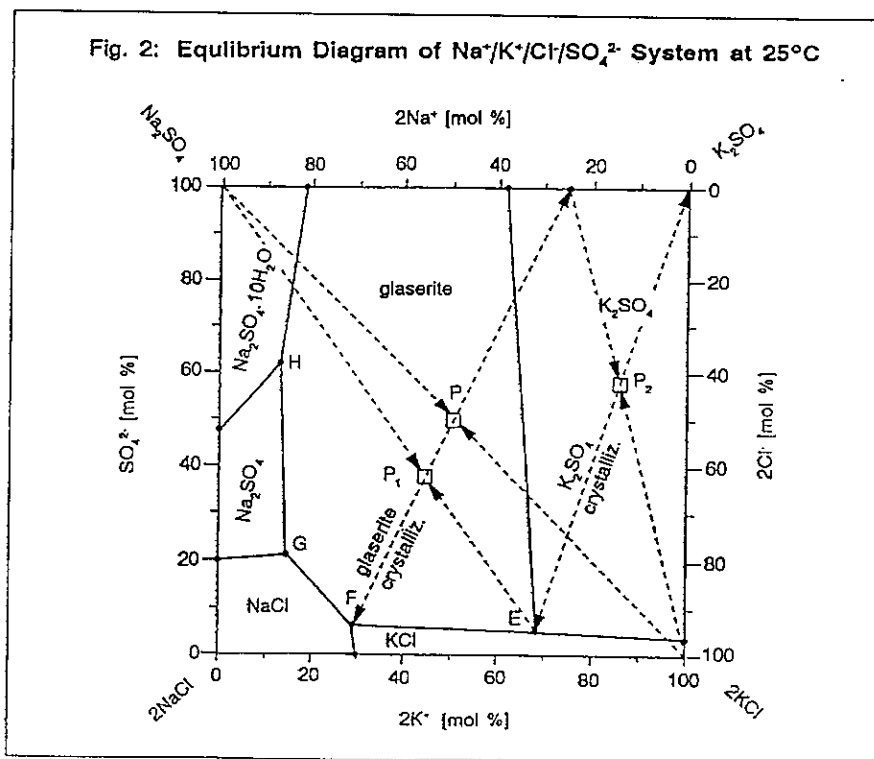
When potassium sulphate is present as a solid phase, the closest it is possible to approach to sodium chloride is a solution which, at +25°C, contains a maximum of 26.8 mol of sodium chloride per

1,000 mol of  $\text{H}_2\text{O}$ , corresponding to 86.9 g  $\text{NaCl}$  per 1,000 g  $\text{H}_2\text{O}$ . Sodium chloride-saturated solutions can only be recovered if the double salt glaserite is first produced as an intermediate and then decomposed. This calls for a two-stage process, which is approximately described by equations (2) and (3):



In these equations the composition of the double salt glaserite is represented as 3 mol  $\text{K}_2\text{SO}_4$  per mol

Fig. 2: Equilibrium Diagram of  $\text{Na}^+/\text{K}^+/\text{Cl}^-/\text{SO}_4^{2-}$  System at 25°C





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modified by reaction with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  to a composition near to G, while further glaserite crystallizes.

- The near-G glaserite mother liquor is cooled to  $0^\circ\text{C}$  thus yielding the amount of Glauber's salt required for the salting-out of glaserite.

- The Glauber's salt mother liquor is evaporated at higher temperatures to yield pure sodium chloride.

- The residual solution of the evaporation process is cooled and the recovered potassium chloride and its mother liquor are recirculated into the glaserite production stage.

Figure 3 is a block flow diagram of the process.

## Process concept and description

### Glaserite production (conversion)

Anhydrous sodium sulphate or Glauber's salt is converted by reaction with potassium chloride to obtain glaserite at ambient temperature in continuously-operating, large-capacity reaction crystallizers (Fig. 4).<sup>7</sup> The raw materials are fed into the glaserite crystal bed and the resultant glaserite is withdrawn as a concentrated crystal suspension and recovered as a crystalline intermediate by treatment in centrifuges or filters. The sodium chloride-rich supernatant liquor, also containing sodium sulphate, is discharged in crystal-free condition and is subsequently used to produce sodium sulphate (as Glauber's salt) and then recirculated to the process. In discharge-free operation, it is used to yield sodium chloride and potassium chloride. The potassium chloride is recirculated to the main process line, whereas the sodium chloride is a marketable by-product.

### Potassium sulphate production (decomposition)

The reaction of the intermediate glaserite with additional potassium chloride to become potassium sulphate is also performed at  $25^\circ\text{C}$

Fig. 4: Glaserite-I and  $\text{K}_2\text{SO}_4$  Crystallization Stages

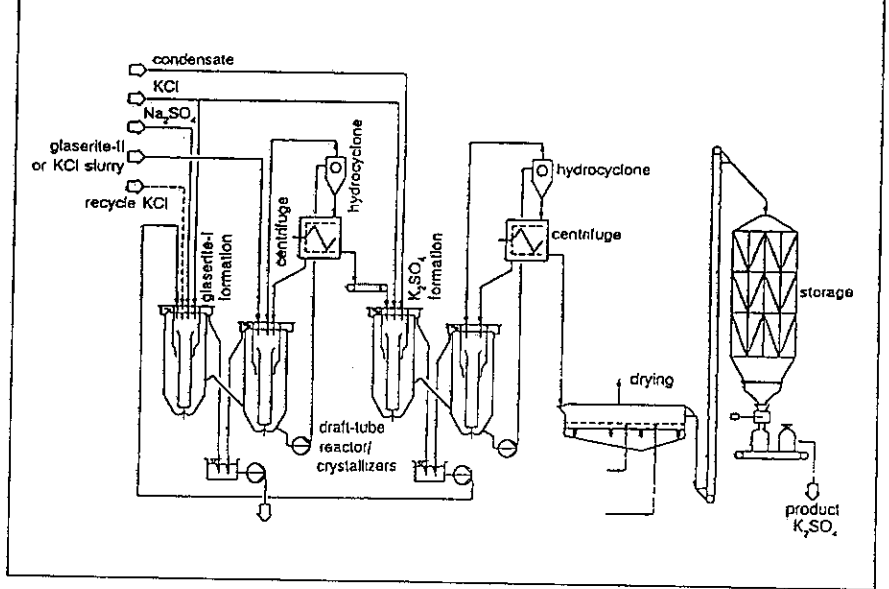


Fig. 5: Secondary Glaserite and Glauber Salt Recovery

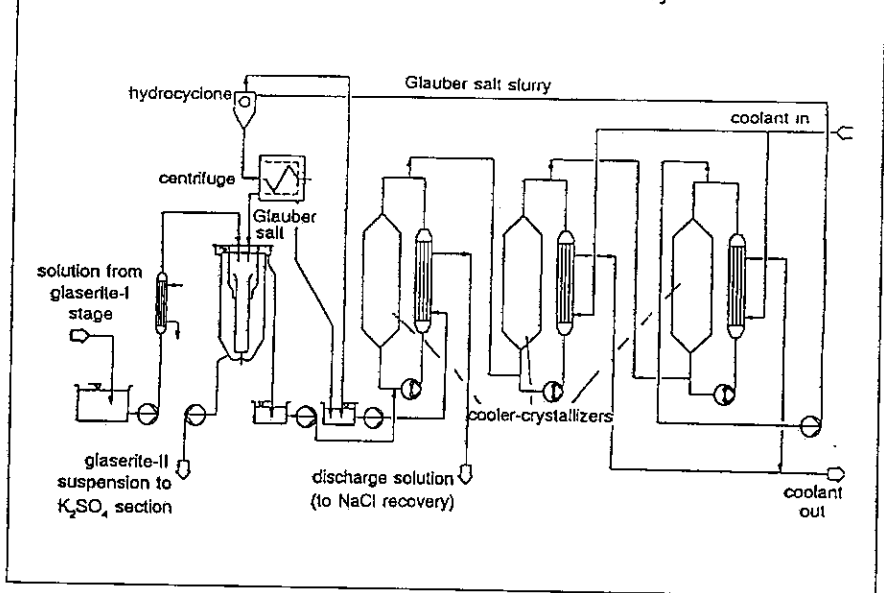
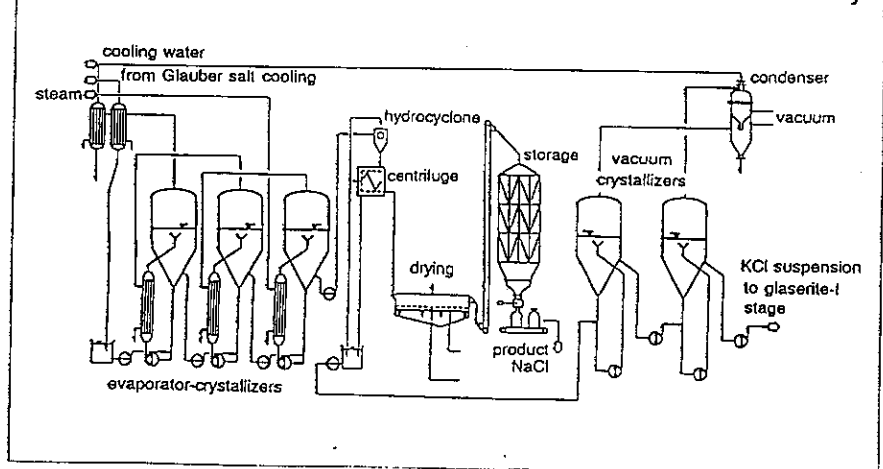


Fig. 6: Sodium Chloride Production and Potassium Chloride Recovery



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in continuously-operating reaction crystallizers (Fig. 4). The potassium sulphate produced is extracted as highly concentrated suspension and separated by means of centrifuges or filters; the separated solution from the reaction crystallizer is recirculated into the process stage of the glaserite production. Countercurrent washing of the solid product with water or potassium sulphate solution yields a highly purified, low-chloride product.

## Glauber's salt and secondary glaserite recovery

Glauber's salt from the cooling/crystallization stage is added to the mother liquor from the glaserite production (conversion) (Fig. 5). This causes crystallization of further glaserite (glaserite II), which is stirred into the decomposition reactor. The mother liquor from the glaserite II production is cooled to approximately 0°C, yielding Glauber's salt (see above). In processes with liquid discharge, the process ends with the removal of the solution from the deep-cooling stage after separation of the Glauber's salt.

## Sodium chloride recovery

In a discharge-free process, it is necessary at the end to remove all water introduced at earlier stages. Accordingly, the desulphatized mother liquor from the Glauber's salt cooling crystallization is continuously concentrated in a multiple-stage evaporative crystallization using steam-heated forced-circulation evaporators until it reaches the potassium chloride saturation point (Fig. 6). The sodium chloride which crystallizes out in the process is separated in centrifuges, washed, dried and packed. In places where the climatic conditions are suitable it would be possible partially to replace the evaporator plant by solar evaporation.

Alternatively, the sodium chloride may be withdrawn in a mixed solution containing mostly potassium chloride with very low concentrations of sulphate and the highest possible sodium chloride concentration. The design of the

reaction section of the plant is almost identical for both processes.

## Potassium chloride recovery

In a multiple-stage vacuum cooling crystallization, potassium

chloride is recovered from the centrifuge filtrate of the sodium chloride evaporation plant. After separation into mother liquor and crystallized mass by means of a centrifuge, the two streams are then recirculated into the process.

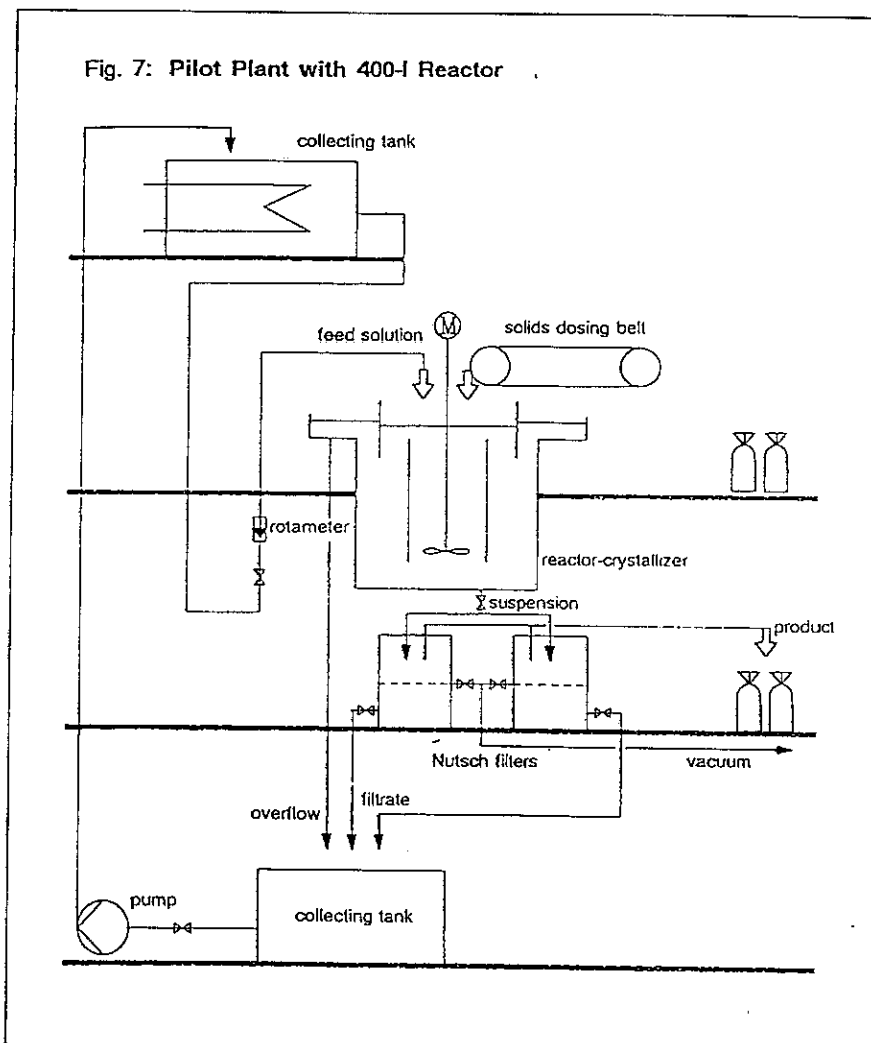


Table II  
Summary Results from Pilot Plant Test Run

	K <sub>2</sub> O yield %	SO <sub>4</sub> yield %	Glaserite mol K/ mol Na	NaCl concentration, g/l	
				actual	theoretical
Glaserite production (with excess KCl)	65.1	92.1	2.7		
mother liquor				215	234
Glaserite production (with excess SO <sub>4</sub> )	69.8	72.4	2.4		
mother liquor				210	245
Complete process cooling + discharge	79.0	95.0			
Glauer's salt					
mother liquor				250	272
K <sub>2</sub> SO <sub>4</sub> mother liquor				64	75

## Results and process characteristics

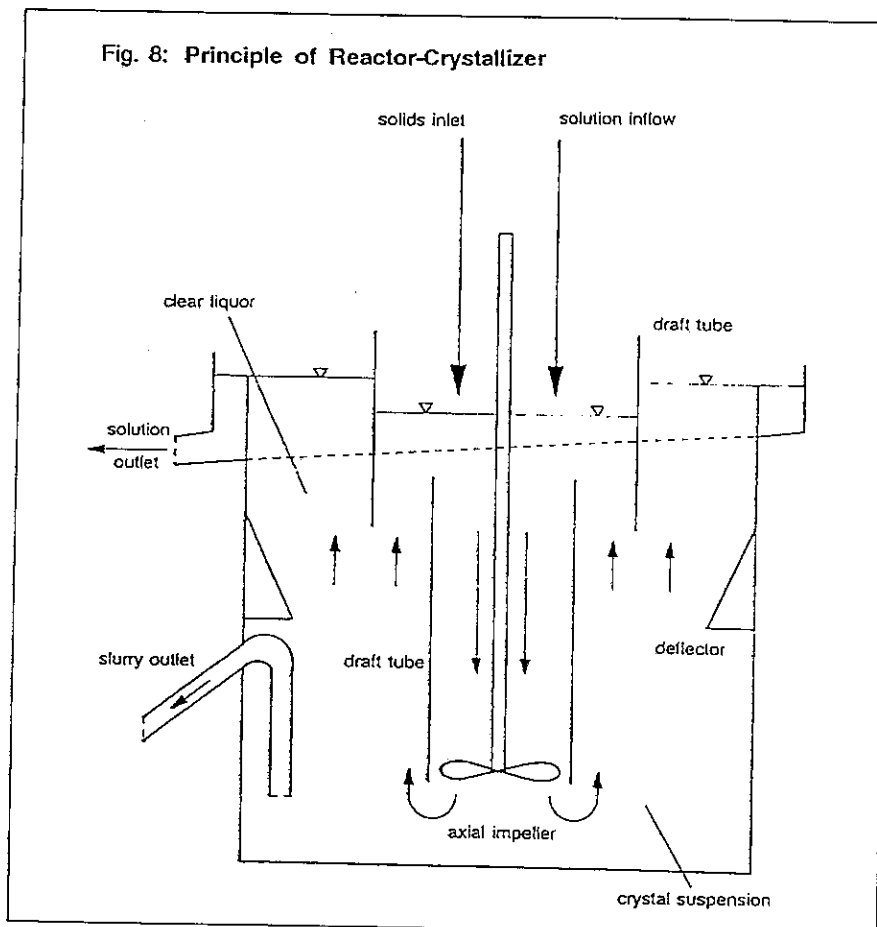
Figure 7 is a schematic view of the pilot plant used to obtain all process-relevant data. The objective was to produce solid glaserite and then solid potassium sulphate from solid potassium chloride and solid sodium sulphate under isothermal conditions. To achieve this necessitated special attention to the following.

- The process should be continuous.
- The compositions in the respective solution phases should as closely as possible reach the equilibrium concentrations E, F and G.
- The highest possible conversion of raw materials should be secured by preventing clogging of the crystal surfaces with reaction product.
- Crystal masses should be coarse-grained to allow easy separation from the liquid phase.
- Apparatus scaling should be prevented.

The task was solved<sup>8</sup> by using special reaction crystallizers with internal circulation by a centrally arranged draft tube (for adjusting the optimum supersaturation) and an integral clarification zone for controlling the solids concentration

in the reaction section (to influence the mean retention time of the crystallized mass). Figure 8 is a simplified diagram showing the functional principle of this apparatus, which can be constructed with capacities of up to 350 m<sup>3</sup>.

In spite of difficult raw material conditions, even when using a clayish, partially-hydrated thenardite, all chemical and physical quality targets were reached in trouble-free, uninterrupted reactor operation over a three-shift test run. This



**Table III**  
Typical Analyses in Messo Potassium Sulphate Process Pilot Tests

	K <sub>2</sub> SO <sub>4</sub> %	Na <sub>2</sub> SO <sub>4</sub> %	KCl %	NaCl %	KCl+NaCl %	H <sub>2</sub> O %	Insolubles %	Density kg/l
<i>Raw materials</i>								
KCl	2.9	-	92.1	4.3		0.2	0.2	
Na <sub>2</sub> SO <sub>4</sub>	2.5	87.7	-	2.2		8.2	2.0	
<i>Process solutions</i>								
Glaserite mother liquor (excess KCl)	-	3.2	10.9	17.3		68.6		1.24
Glaserite mother liquor (excess SO <sub>2</sub> )	-	6.4	7.4	16.8		69.4		1.25
Glauber's salt mother liquor	-	0.8-1.4	6.7-7.0	18.4-20.3		74.1-71.3		1.22-1.23
K <sub>2</sub> SO <sub>4</sub> mother liquor	-	1.6	20.9	5.3		72.2		1.20
<i>Intermediate and final products</i>								
Glaserite	72.5-74.2	22.7-23.5			0.3-0.8	1.1-1.5	1.9-2.6	
Crude K <sub>2</sub> SO <sub>4</sub>	87.5-92.1	0-2.4			1.9-4.3	2.6-6.7	1.9-2.7	
Pure K <sub>2</sub> SO <sub>4</sub>	96.0-98.0	-			0.4-0.6	<0.5		

test run provided practical corroboration of the findings of the research studies<sup>9-12</sup> conducted in the years 1985-1988 at the Potash Research Institute in Sondershausen, Germany.

Table II gives a general survey of the most important values and test results obtained in the test run. This table shows that it was possible to achieve a balanced mass balance in all stages.

The graph in Fig. 9 is the screen analysis profile of the final product potassium sulphate.

Tables III and IV comprise typical analyses and process data. The actual consumption figures deviate only slightly from the theoretical consumption figures.

The by-product sodium chloride is recovered as pure sodium chloride of evaporated-salt quality and may be used either as table salt or for industrial purposes, such as electrolysis.

The process has the following advantages.

- No waste products or effluent solutions discharged
- Reactions at low temperatures
- Continuous process flow
- High yield
- Pure products
- Simple process control and thus high operational reliability
- Ability to accept sodium sulphate of less purity
- Adaptability to local conditions.

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(Not all of these citations are specifically referred to in the text)

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**Table IV**  
Consumption and Production Rates  
(per tonne  $K_2SO_4 - 50\% K_2O$ )

	Without discharge	With discharge
$Na_2SO_4$ consumption, t	0.8	1.0
KCl consumption, t	0.8	1.2
NaCl production, t	0.6	nil
Liquid discharge, m <sup>3</sup>	nil	2.8
Water evaporation, t	2.2	nil

Fig. 9: Crystal Size Distribution of  $K_2SO_4$  Product

