

# ISMA\* Technical Conference

Orlando, Florida, USA  
23-27 October 1978

*\*In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

## EXPERIENCES IN PHOSPHORIC ACID PRODUCTION WITH HEMI-DIHYDRATE AND DIHYDRATE PROCESS

E. Uusitalo, M. Loikkanen, T. Karjalainen and E. Hänninen  
Kemira Oy, Finland

### 1 INTRODUCTION

There exists relatively little published material about the production of strong phosphoric acid with two-stage methods in plant scale. The phosphoric acid plant of Kemira Oy at Siilinjärvi, Finland has used for several years both a hemi-dihydrate and a dihydrate process with Kola phosphate as raw material. This paper summarizes our experiences from that period.

The Siilinjärvi plant was constructed in 1969 and used the hemi-dihydrate process until end 1973. The nominal capacity was 75 000 t  $P_2O_5$ /a and concentration of the product acid ca 42 %  $P_2O_5$ . Owing to increasing demand for phosphoric acid the hemi-dihydrate process was altered to dihydrate process in 1973. The decision was made after comparing the various process alternatives. The minimum fluorine content in the air inside the plant as required by industrial hygiene was one of the factors that made us select the dihydrate process.

The modification was based on the company's own know-how and engineering. The new capacity is 120 000 t  $P_2O_5$ /a and  $P_2O_5$  concentration of the acid 30 %. A facility was built for the concentration of the acid. The water recirculation system of the plant is completely closed and includes also the waters of the gypsum area. This system makes possible the production of phosphoric acid even under the strictest regulations on environmental protection.

### 2 HEMI-DIHYDRATE PROCESS

#### 2.1 Process description

The principle of the process is described in Appendix 1. In the first process stage a multitank reactor chain was used where calcium sulphate crystallized at 75-80 °C as hemihydrate. The hemihydrate was filtered with a tilting pan filter and recrystallized as dihydrate at 50 °C and  $H_2SO_4$  concentration of 5 %. The filtering of hemihydrate produced phosphoric acid with a  $P_2O_5$  concentration of 42-44 %. Recrystallized gypsum was filtered through the other half of the same filter and conveyed filter moist to the storage area. Only Kola phosphate was used as raw material.

#### 2.2 General observations on the process

Owing to certain difficulties in the process, the first year production was only about a half of the nominal capacity. Later, production corresponded to consumption and in the last few years it was close to 80 000 t/a  $P_2O_5$ .

The efficiency of the process, 94-95 % was lower than expected (98 %). The reason for this was that only 45-50 % of the hemihydrate was converted to dihydrate in the process and consequently only a corresponding amount of coprecipitated  $P_2O_5$  was liberated. Another factor deteriorating the efficiency was the poor filterability of gypsum after the recrystallization.

A little less than a half of the  $P_2O_5$  losses of gypsum was coprecipitated  $P_2O_5$  and the rest watersoluble  $P_2O_5$ .

Owing to the slowness of the recrystallization the slurry was handled and filtered in a state of constant conversion. This caused clogging in various stages of the process. In addition the two-stage process was quite complicated, which added to its sensitiveness. A disturbance in the hemihydrate stage provoked others in the recrystallization stage and vice versa.

The good filterability of dihydrate gypsum is usually mentioned as one advantage of the hemi-dihydrate process, whereas the filtering of hemihydrate is considered more difficult. In the Siilinjärvi process however the situation was the opposite. The filterability of hemihydrate was clearly better (about  $8 \text{ t } P_2O_5/m^2/24 \text{ h}$ ) than that of dihydrate gypsum. The crystals were well formed (Figure 1).

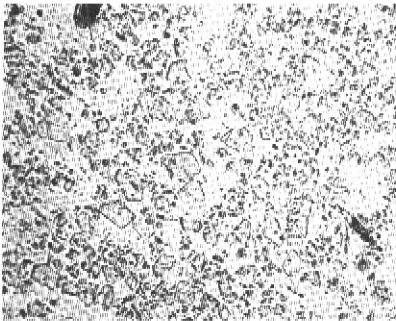


Fig. 1 Hemihydrate crystals in reaction slurry (128 x)

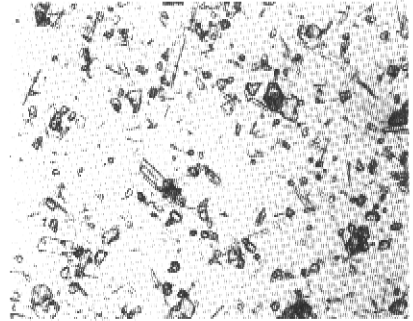


Fig. 2 Hemi- and dihydrate crystals in recrystallization slurry (150 x)

Recrystallization of hemihydrate normally gives crystals with good filtering properties; with Kola phosphate the crystals were of different sizes, which disturbed filtration (Figure 2).

At its best the concentration of the product acid was as high as 44 %  $P_2O_5$ . In practice the concentration was kept at 40-42 % because the coprecipitated  $P_2O_5$  of hemihydrate gypsum grew together with the concentration. The product acid was purer than dihydrate acid as concerns for example the following impurities: Ca,  $SO_4^{2-}$ , Al and Na.

The quantity of solids was only ca 0.5 % and postprecipitation negligible. The precipitate contained in the acid however hardened in the storage tanks and had to be broken off a couple of times per year. A typical composition of settlings in a storage tank was 55 % of  $CaSO_4$ , 41 % of alkali silicofluorides (as  $K_2SiF_6$ ) and 4 % of phosphates.

Fluorine was recovered in connection with the vacuum cooling of reaction slurry. It gave fluosilicic acid of the following kind:

$H_2SiF_6$	16 %
Solids ( $SiO_2$ )	2 %
$P_2O_5$	0.3 %

### 2.3 Waste gypsum

The final recrystallization of gypsum took place in the waste gypsum storage area. Figures 3 and 4 show the conversion of the dihydrate percentage and insoluble  $P_2O_5$  in the gypsum hill. The conversion period was 10-12 days. During that coprecipitated  $P_2O_5$  was freed from the crystal lattice and the amount of insoluble  $P_2O_5$  dropped to ca 0.1%. Watersoluble  $P_2O_5$  concentrated inside and on the bottom of the hill and by and by returned to the process via the water recirculation system. This means that the gypsum in the hill is very pure. In recrystallization the gypsum however hardens and must therefore be quarried out and ground before eventual utilization.

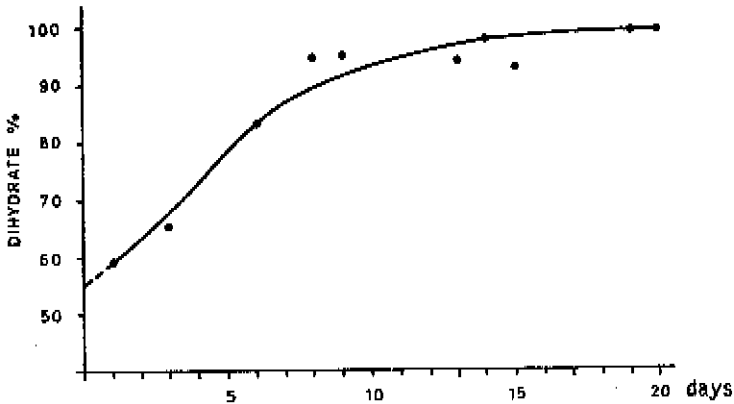


Fig. 3 Conversion of hemihydrate to dihydrate in gypsum hill.

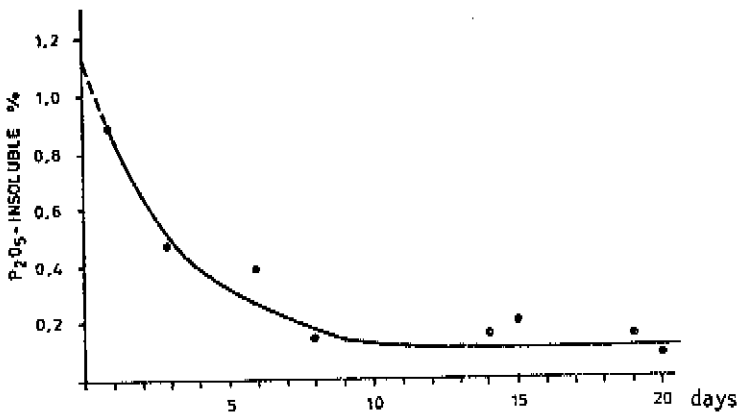


Fig. 4 Conversion of  $P_2O_5$  insoluble in gypsum hill.

## 2.4 Recrystallization

The main reason for the problems in the process was the raw material, Kola phosphate, which in fact did give excellent hemihydrate, the conversion of hemihydrate to dihydrate however being too slow. The hemihydrate obtained from Kola phosphate required 2-3 d for recrystallization in process conditions, whereas for example with Morocco and Florida phosphates 0.5-1 h is sufficient. Poor recrystallization meant that coprecipitated  $P_2O_5$  remained in the waste gypsum.

Figures 5 and 6 show the change of the dihydrate percentage and the conversion of insoluble  $P_2O_5$  in the reaction slurry.

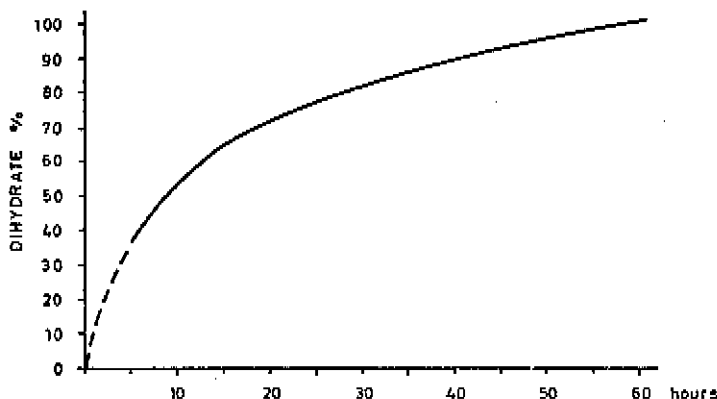


Fig. 5 Conversion of hemihydrate to dihydrate in reaction slurry.

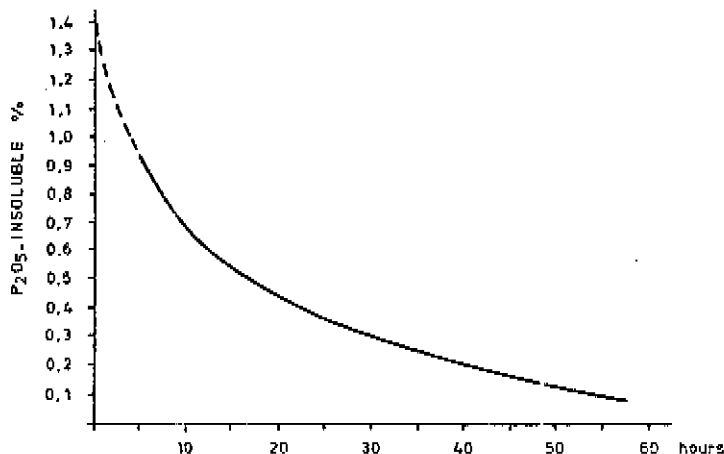


Fig. 6 Conversion of  $P_2O_5$  insoluble in gypsum in reaction slurry.

Recrystallization in pure water or circulating water in sufficiently weak suspension (1:20) converted also Kola hemihydrate to dihydrate within 1-2 h. In this dilution for ex. the rare earths contained in the hemihydrate remain for the most part in the solution. Figure 7 describes the conversion of hemihydrate to dihydrate in the circulating water of the phosphoric acid plant.

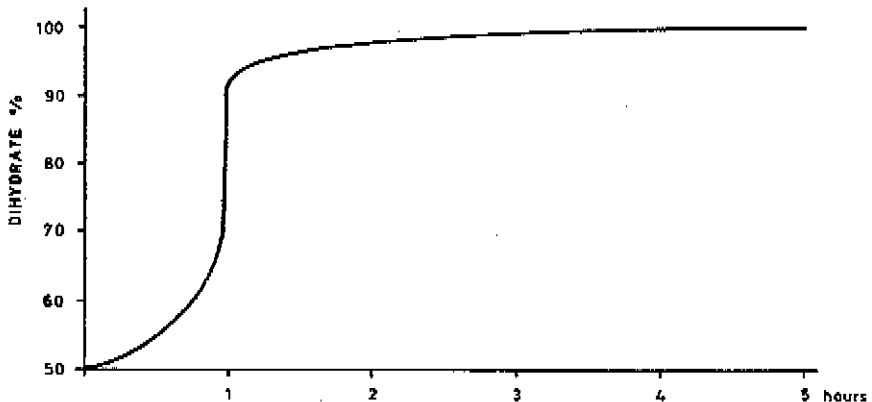


Fig. 7 Conversion of hemihydrate to dihydrate in circulating water of process.

A reason for the problematic recrystallization is obviously the rare earths contained in Kola phosphate (La 0.22 %, Ce 0.36 %). By adding rare earths to the recrystallization solution recrystallization can be prevented entirely. The possible effect of strontium is covered by that of rare earths. One of the other factors that may have an effect is aluminium.

It has not been studied as what kind of compounds  $Ce^{+4}$  and  $La^{+3}$  occur in the hemihydrate phase. The fact is however that they mainly occur in insoluble form. In recrystallization they more or less dissolve into ion form, hampering the recrystallization of gypsum.

The use of certain additives and crystal nuclei was tried in plant scale and in laboratory. The addition of fluoride was the only one that showed any significant effect. The influence of fluorine is based on the fact that it precipitates cerium and binds  $Al^{+3}$  and  $La^{+3}$  ions as stable fluoride complexes. Thus the rare earths do not disturb recrystallization.

The experiments showed that fluorine must be added until there is an equivalent amount to precipitate La, Ce and Al as fluorine compounds and bind silicon as  $SiO_2$ . The amount above all depends on how much silicon the apatite contains because silicon consumes most of the fluorine and its amount is greater than that of rare earths and aluminium. The amount of silicon also varies much more than the other impurities. In Kola phosphate the  $SiO_2$  content may vary from 0.5 to 2.3 %.

Fluorine can be added as  $CaF_2$ , NaF and  $NH_4F$  compounds. The fluorine contained in the fluosilicic acid recovered in the process was thought to form the

source of extra fluorine needed for improving recrystallization. Fluosilicic acid can be hydrolysed with ammonia to ammonium fluoride.

The effect of the fluoride amount on the conversion of hemihydrate to dihydrate is described in Figure 8.

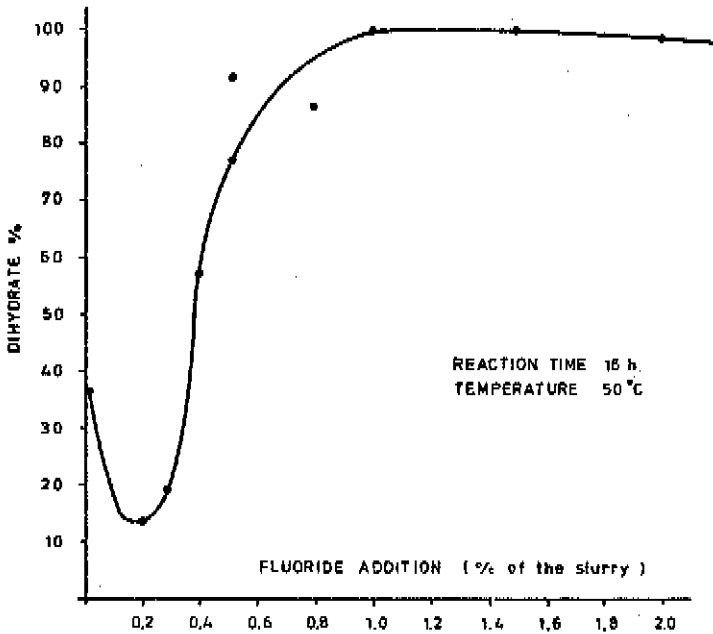


Fig. 8 Effect of fluoride on conversion of hemihydrate to dihydrate.

Figure 9 shows the effect of the fluoride amount on the conversion rate.

Figure 10 contains the La and Ce concentrations analyzed by means of neutron activating from filtrates of the phosphoric acid plant. The figure also gives the Al concentrations, which except for strong filtrates vary like the rare earth concentrations.

Normally the dihydrate crystals formed in the process were long and needle-like. A fair amount of extra fluorine (ca 2 % of apatite quantity) made the crystals long and relatively broad, while a large amount (ca 4.5 % of apatite quantity) caused them to be short and thick (Figure 11). Thus it can be assumed that additional fluoride has a favourable influence on the amount of watersoluble  $P_2O_5$  as well.

An  $NH_4F$  amount corresponding to the  $H_2SiF_6$  production of the process would have sufficed to raise the share of dihydrate to 90 %. Tests and calculations however showed that the cost of fluorine addition would have been too high.

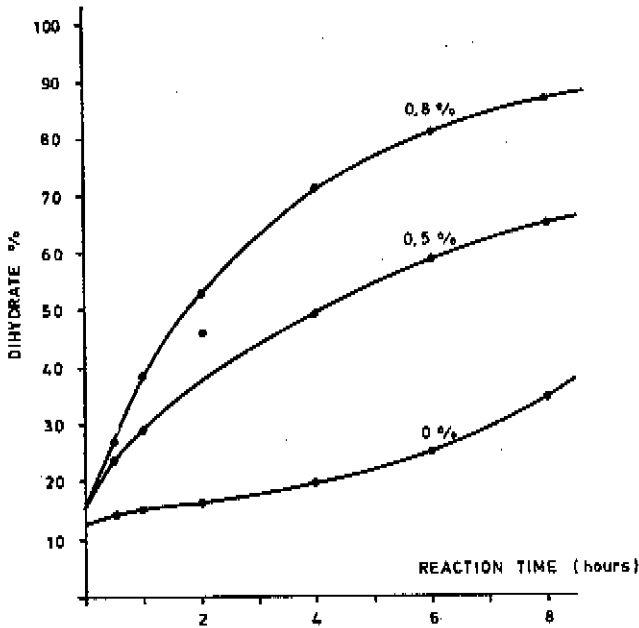


Fig. 9 Effect of fluoride on conversion rate.

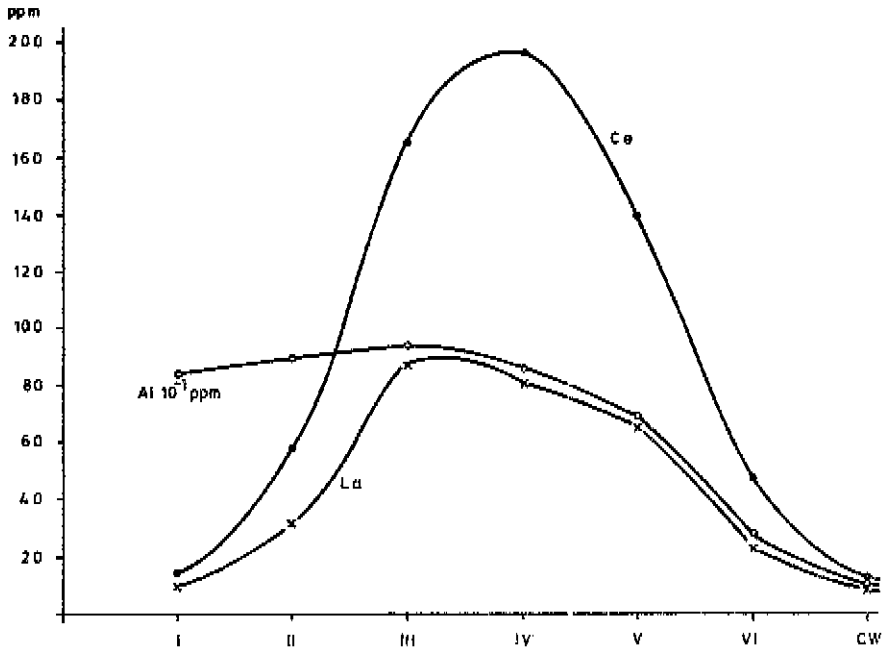


Fig. 10 La, Ce and Al concentrations in filtrates of hemi-dihydrate process.



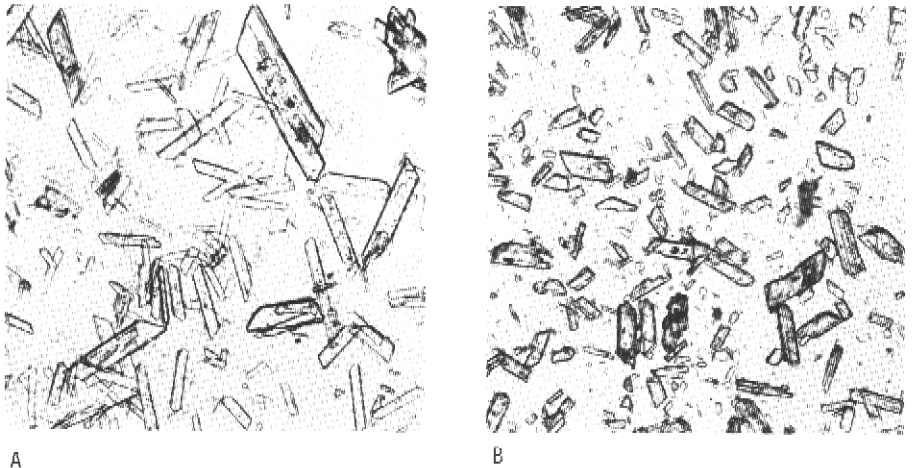


Fig. 11 Effect of fluoride amount on crystal shape (150 x).

A = fluoride addition 2 % of apatite amount  
 B = " " 4.5 % " "

With some other raw material the process would probably have been more successful. It must nevertheless be remembered that with all raw materials impurities accumulating in the closed water system may hamper the crystallization of gypsum.

## 2.5 Problems concerning the equipment

The reason why the hemi-dihydrate process caused certain surprises to the equipment designers was that clogging in the different steps of the process was unexpectedly heavy. Some examples of the problems due to gypsum:

- The process piping had not been equipped with a sufficient number of flange joints that would have made cleaning easier.
- Besides from pipes, gypsum had to be constantly removed from reactors, reactor channels, filter, gypsum and washwater funnels, filtrate tanks, gypsum conveyors, phosphoric acid storage tanks, etc. In all these it was necessary to make constructional modifications to prevent clogging or to facilitate cleaning.
- Hardened gypsum also damaged the mixers of phosphoric acid storage tanks and the construction of the mixers had to be altered. The heaviest clogging caused by gypsum occurred in the recrystallization step and after it.

In addition, the precipitation of  $\text{Na}_2\text{SiF}_6$  caused clogging in the second filtrate pipes, where the concentration of phosphoric acid was 30 %  $\text{P}_2\text{O}_5$ .

$\text{SiO}_2$  precipitated in the reactor gas outlet, which necessitated wider ducts and the construction of an efficient water rinsing system.

All these equipment modifications raised considerably the maintenance costs of the first few years of operation.

### 3 DIHYDRATE PROCESS

The flowsheet of the dihydrate process is in Appendix 2. The main jobs required by the change of process were modifications to the pipings and reorganization of the filter areas. In addition a concentration plant was built. The process change succeeded very well. The efficiency of the plant with Kola phosphate is now over 97 %.

The Siilinjärvi plant is situated in the middle of a beautiful lake district, and this means extremely strict environmental restrictions. The fairly shallow lakes tolerate no extra phosphorus and the forests are sensitive to fluorine pollution. Therefore the wastewaters of the entire plant and plant area are led into a closed water circuit. The quantity of circulation water is 1 600 m<sup>3</sup>/h. Phosphorus emission to the watercourse is about 2 kg P/d at a production capacity of 400 t P<sub>2</sub>O<sub>5</sub>/d.

### 4 COMPARISON BETWEEN HEMI-DIHYDRATE PROCESS AND DIHYDRATE PROCESS

#### 4.1 Development of the efficiency

The hemi-dihydrate process was unstable and the efficiency kept fluctuating 2-4 %-units, sometimes even more. The problems in the process are described in Figure 12, which gives the weekly efficiency averages during a couple of months in the first year and the corresponding figures the year after. It can be said that after the initial problems the process was mastered clearly better. The average efficiency of the hemi-dihydrate process calculated from the raw material consumption was 94-95 %, which was more or less the same as calculated from the analysis results. At its best the efficiency was 97 %, calculated from the analysis.

The efficiency of the dihydrate process with Kola phosphate is above 97 %.

The annual production and development of the efficiency are in Figure 13. The low production in 1976 is due to the decrease in demand that followed the general recession.

Raw material costs have been compared with the total costs of 1977 in Figure 14. The raw material price corresponds to the 1978 level.

#### 4.2 Energy costs

The consumption of steam and electricity as today's price is presented in Figure 15.

#### 4.3 Other variable costs

See Figure 15.

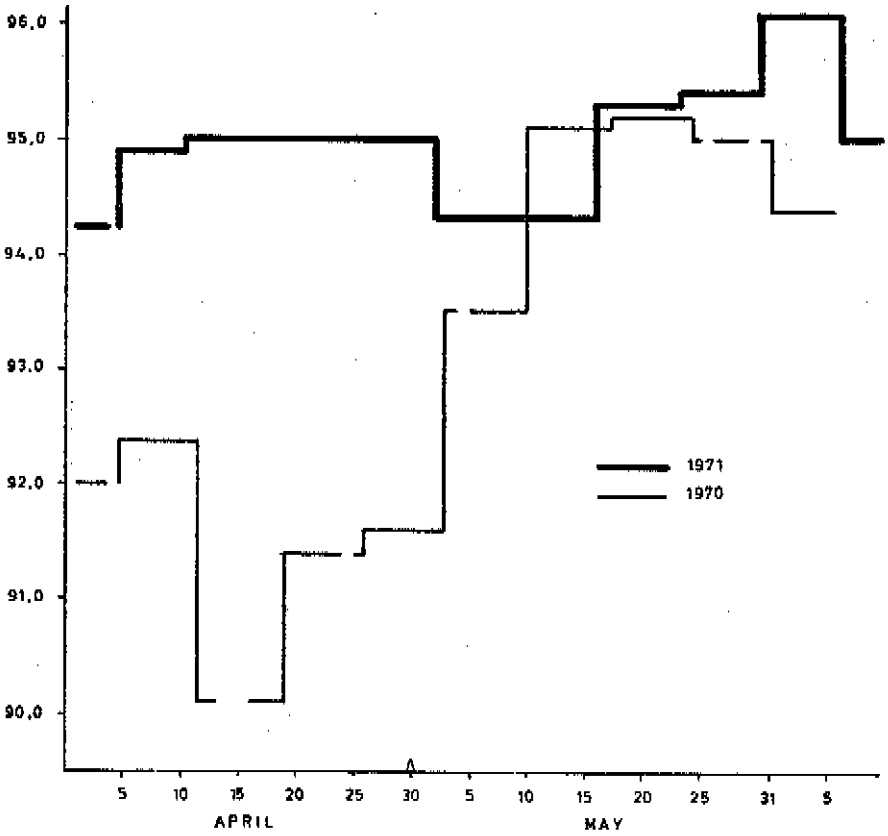


Fig. 12 Examples of weekly efficiencies in 1970 and 1971.

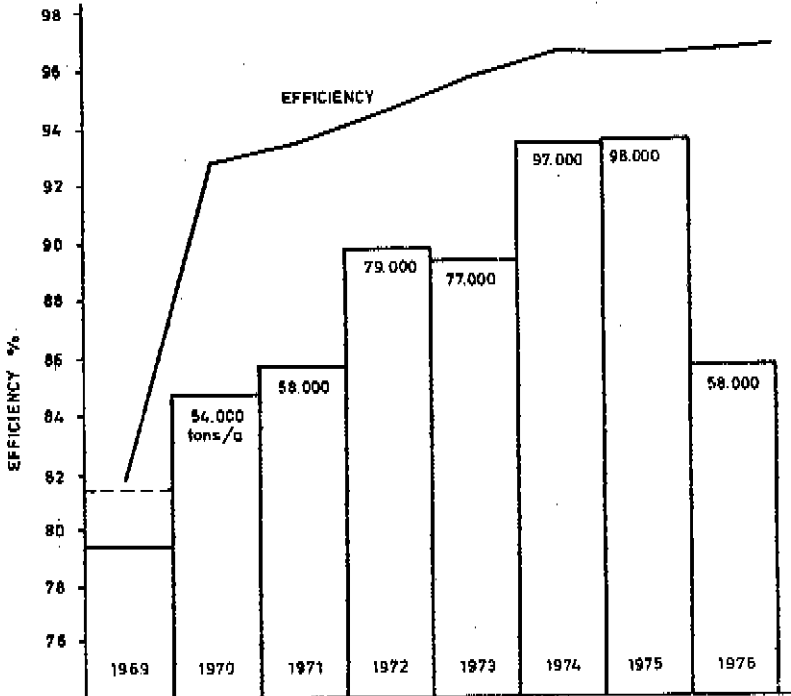


Fig. 13 Development of efficiency and annual production of the plant.  
Process modification at the end of 1973.

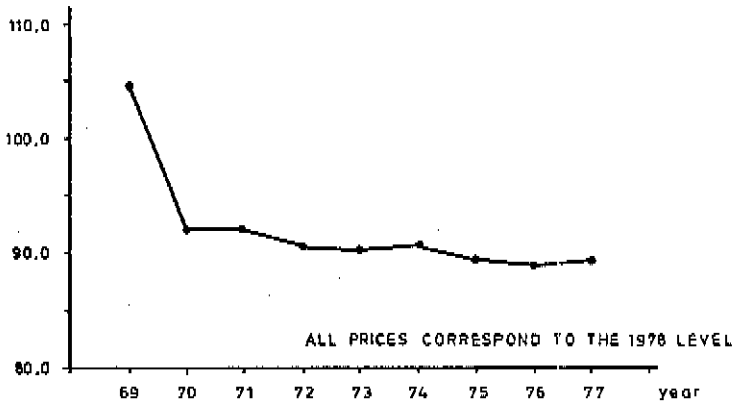


Fig. 14 Raw material costs compared with total costs (1977 total costs = 100). Process modification at the end of 1973.

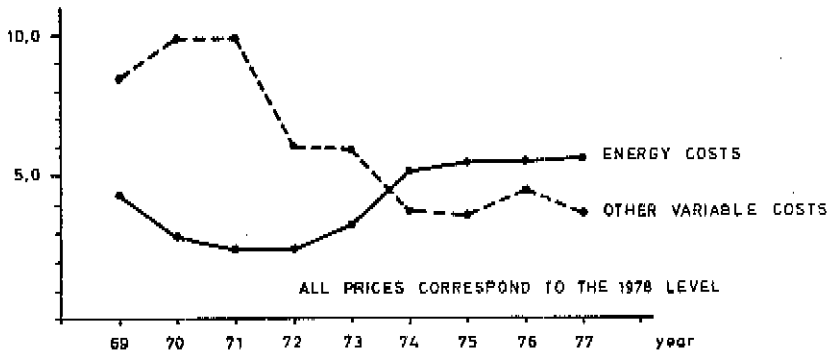


Fig. 15 Energy costs and other variable costs compared with total costs (1977 total costs = 100). Process modification at the end of 1973.

#### 4.4 Total production costs

Figure 16 shows that once the process began to run smoothly the costs of the hemi-dihydrate process and dihydrate process + concentration were roughly the same. The simpler dihydrate process however is far less troublesome.

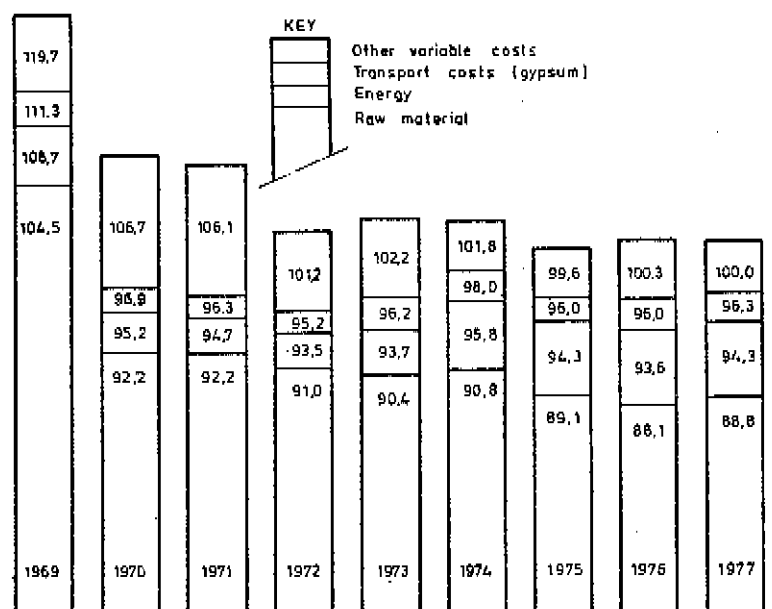


Fig. 16 Cumulative total production costs compared with 1977 total costs (= 100). All prices correspond to 1978 level.

#### 4.5 Disturbance stoppages

The annual stoppage hours due to process disturbances are in Figure 17.

#### 4.6 Industrial hygiene

From the personnel's point of view the worst problem in the hemi-dihydrate process is the fluorine contained in the plant air. Fluorine liberates in the process as HF and  $\text{SiF}_4$  compounds. The weaker the acid the larger the relative amount of  $\text{SiF}_4$  liberated, which hydrolyzes with water and forms  $\text{H}_2\text{SiF}_6$  and  $\text{SiO}_2$ . If there is not sufficiently HF to dissolve  $\text{SiO}_2$ , it remains undissolved. Normally, at a  $\text{P}_2\text{O}_5$  concentration of 46 %, a state of balance is reached in which  $\text{SiO}_2$  does not occur. At over 46 %  $\text{P}_2\text{O}_5$  concentrations, free HF occurs in the  $\text{H}_2\text{SiF}_6$  produced.

In process conditions  $\text{SiO}_2$  precipitated in the gas ducts and caused clogging, which again resulted in an excessive fluorine content in the plant air. During the hemi-dihydrate process it was difficult to maintain the fluorine content of the plant air below  $2.5 \text{ mg F/m}^3$  in spite of the fact that the gas ducts were cleaned of  $\text{SiO}_2$  precipitate once a week. With the present dihydrate process the fluorine content has been under  $0.5 \text{ mg/m}^3$ . The gas ducts are cleaned only a few times per year.

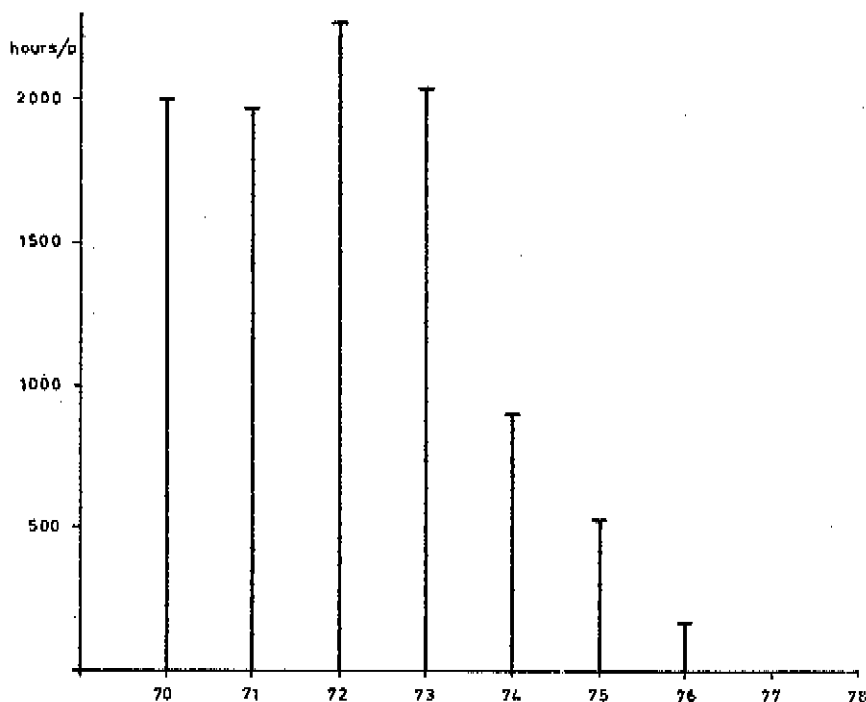


Fig. 17 Disturbance stoppages.

#### 4.7 Utilization of product acids in fertilizer production

The MAP that was produced with acid from the hemi-dihydrate process differed quite essentially from the MAP made with acid from the dihydrate process. Hemi-dihydrate MAP was pulverous and tended to harden. Dihydrate MAP was granular and did not harden easily. Its granulating properties in fertilizer manufacture were also much better than those of hemi-dihydrate MAP.

Some MAP analyses (percent by weight)

Raw material	H <sub>2</sub> O	NH <sub>4</sub> -N	P <sub>2</sub> O <sub>5</sub>	F	Ca	Al	Fe	Si
Acid from hemi-dihydrate process	3.2	11.1	53.9	1.37	0.08	0.17	0.56	0.11
Acid from dihydrate process	6.4	10.9	50.6	1.32	0.32	0.34	0.51	0.23

Both MAP grades contained about 7.5 % of insoluble matter.

The Al content of MAP increases to 2- or 4-fold and insoluble phosphates change from crystalline to amorphous when the dihydrate process is used.

## 5 GENERAL

The above comparison shows how important it is, when selecting the process, to know the properties and behaviour of different raw phosphates.

The suitability of a raw phosphate for phosphoric acid production can be only roughly estimated by phosphate analysis. The only reliable method to test a raw phosphate is to produce phosphoric acid from it. These tests can be made in laboratory or pilot plant scale and they define the factors that are the most important for the design and feasibility of the plant.

Kemira usually tests the raw phosphates it buys for its own phosphoric acid plants. Also the development of the company's own phosphate mine has required quite a number of tests connected with both phosphoric acid and fertilizer production.

Environmental protection and waste problems are having more and more to say on the future of phosphoric acid processes. A closed water recirculation system prevents the waste waters of the process from escaping into the environment. At the same time the problems caused by impurities gathering in the water of the recirculation system and disturbing the crystallization and filtration of gypsum must be solved. Kemira has been satisfied with the solutions that are in use in its plants and that make possible production without pollution.

## 6 SUMMARY

This paper compares the production of ca 42 %  $P_2O_5$  phosphoric acid with hemi-dihydrate and dihydrate process, with Kola phosphate as raw material.

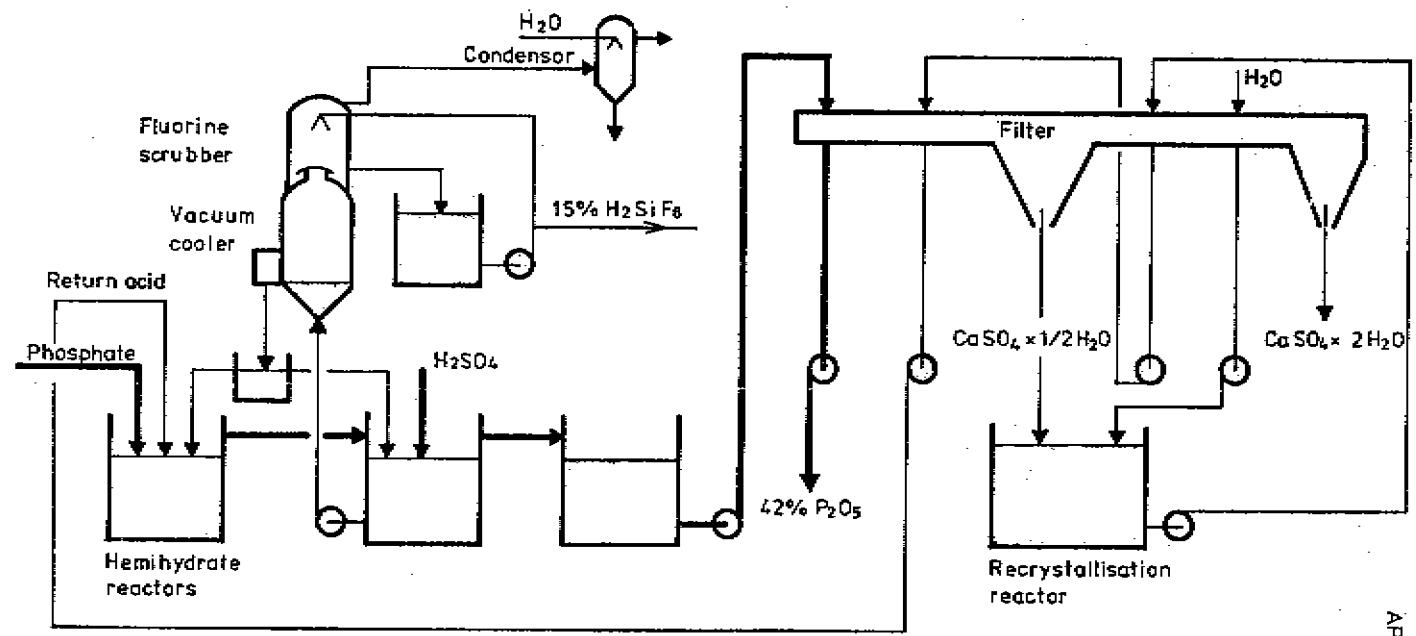
In the hemi-dihydrate process the rare earths contained in Kola phosphate slowed recrystallization so that only about a half of the hemihydrate was converted to dihydrate in the process. This lowered the efficiency from the target value 98 % to 94-95 %. In addition the handling of reaction and gypsum slurries under continuous conversion disturbed operation. It was observed that the addition of fluoride made it possible to precipitate the rare earths as fluorine compounds in the recrystallization stage, which improved essentially the rate of recrystallization. The fluoride amount needed however depends for ex. on the  $SiO_2$  content of the raw phosphate. In process conditions the necessary fluoride amount would have been so high that the addition of fluoride would not have been economically feasible.

The advantages of the hemi-dihydrate process over the dihydrate process were stronger and purer acid and the possibility later to recover most of the phosphorus from the waste gypsum in the storage area by means of the water recirculation system. The disadvantages of the hemi-dihydrate process were its complicity and the high cost of maintenance, cleaning and handling of gypsum. The production costs of strong acid were roughly the same for both. The simpler dihydrate process however is easier to operate and the problems concerning industrial hygiene caused by fluorine are also less troublesome.

Analyzing the difficulties related to the hemi-dihydrate process, converting it to dihydrate process and searching the optimum environmental protection methods have been technically very demanding. These experiences have given Kemira valuable information for the development of new one-stage and two-stage processes.



HEMI - DIHYDRATE PROCESS  
 KEMIRA OY SIILINJÄRVI FINLAND



APPENDIX 1

DIHYDRATE PROCESS AND ACID CONCENTRATION  
KEMIRA OY SIILINJÄRVI FINLAND

