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ENVIRONMENTALLY AND ECONOMICALLY BALANCED  
PHOSPHORIC ACID AND FERTILIZER COMPLEXES

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SUMMARY

Taking into account all by-product aspects of new or existing chemical complexes will be resulting in environmental and economical optimal systems.

Starting from single processes as part of a phosphoric acid and fertilizer complex the paper tries to show useful combinations to convert waste and by-products into useful products.

But looking over the own fence will offer sometimes further advantages as it is shown in a joint venture project for aluminium fluoride between an aluminium smelter and a phosphoric acid complex as supplier of the raw material fluosilicic acid.

## 1. INTRODUCTION

The phosphate fertilizer industry is growing faster worldwide year by year. More and more of the basic  $P_2O_5$ -plants are being announced and units with a capacity of 1 500 t/d  $P_2O_5$  are already common.

Slide No. 1 is showing us the world trend in the phosphoric acid production and for the related by-products. One can see that we cannot anymore afford us to dump or to emit the tremendous amount of produced by-products and emitted fluorine without damaging the environment for ever.

Slide No. 2 is showing the restrictions on fluorine emission and for solids disposal in some countries and also actual figures of phosphoric acid plants. Anyway the total fluorine emission from a fertilizer complex is the main consideration in pollution control.

The Chemie Linz plant site of the fertilizer complex you can see it in slide No. 3. As you see the plant site is very near to the river Danube ("for it's blue the Austrians are standing for") and also to the city Linz. Chemie Linz have been already operating for years an environmentally and economically balanced complex, which allows Chemie Linz to contribute a number of processes for by-product conversion and related know-how to the solution of these problems.

The complexity of a chemical complex makes it rather difficult for the project engineers to be aware of all details of the particular process and possible common environmental and economical solutions. But for the future we have to consider more and more complete systems to be able to hold on the declining quality of the environment.

The following details will assist you in considering possible combinations of processes to improve the environmental and economical situation of your chemical complex.

## 2. AVAILABLE PROCESSES WHICH ARE FITTING INTO THIS CONCEPT

The available processes which are fitting into this concept are summarized in four groups as basic processes, gypsum accepting processes, fluorine accepting processes and other processes which are offering useful combinations with the other groups.

The following figures are generalized and they should show only the tendency. For an exact overall balance for a complex the actual used rock phosphate and the process particularities have to be taken into account.

Slide No. 4 is showing us the datas on basic processes:

### 2.1 BASIC PROCESSES

#### 2.1.1 PHOSPHORIC ACID PROCESS

##### 2.1.1.1 Dihydrate process

(acid from 28 to 32 %  $P_2O_5$  will be obtained)

Available processes:

DORR-OLIVER

FISONS

PRAYON

PSG-UCB (PECHINEY SAINT GOBAIN - UNION CHIMIQUE

BEDRIJVEN S.A.)

SINGMASTER & BREYER

RHONE - PONLENC

By-products:

a) Phospho-gypsum, approx. 5 t/t  $P_2O_5$   
(as dry dihydrate)

b) Fluosilicic acid, approx. 7 kg/t  $P_2O_5$   
(as F from attack section)

ad.a) Special know-how (e.g. from Chemie Linz) is necessary to reduce the fluorine and  $P_2O_5$  content to allow further use of the phospho-gypsum in the sulphuric acid and cement as well

as for the ammonium sulphate production. The phospho-gypsum may be also used for adjusting the retard setting of the cement. If the phospho-gypsum gets recrystallized it will be also acceptable for the production of wall boards and plaster of Paris.

ad.b) This fluorine is normally emitted with the waste water, but in a balanced complex it may be well utilized as an additional raw material source for aluminium fluoride or fluosilicate production.

#### 2.1.1.2 Hemihydrate-dihydrate process

(acid from about 30 % will be obtained)

Available processes:

MITSUBISHI

NISSAN

NKK

By-products:

a) Phospho-gypsum, approx. 5 t/t  $P_2O_5$   
(dry dihydrate)

b) Fluosilicic acid, approx. 7 kg/t  $P_2O_5$   
(as F from attack section)

ad.a) Normally this phospho-gypsum may be used without any special treatment for adjusting the retard setting of the cement or for the production of sulphuric acid and cement as well as after partial calcination as plaster of Paris.

ad.b) Comments equal to the ones for the dihydrate process.

Acid with 42 % - 50 %  $P_2O_5$  will be obtained directly with the newer processes from FISON'S (HDH) or NISSAN C. Experience about the possible conversion of this by-product-gypsum is not available.

#### 2.1.1.3 Hemihydrate process

(acid from about 38 to 42 % or more will be obtained)

Available processes:

there are developments from

ALBATROS, FISON'S, HEURTEY, LANDSKRONA, NORDENGREN.

The older processes have been causing some operational problems and they have been seldom applied inspite of the advantage of the more concentrated acid.

By-products:

- a) Phospho-gypsum, approx. 3,9 t/t  $P_2O_5$   
(as dry hemihydrate)
- b) Fluosilicic acid, 7 kg/t  $P_2O_5$   
(as F from attack section)
- ad.a) Special know-how for reducing the fluorine and  $P_2O_5$  content is essential for further use in gypsum sulphuric acid plant. The high impurities (mainly  $P_2O_5$ ) may also cause problems when used for the conversion to ammonium sulphate (filter stage).
- ad.b) Comments equal to the ones for the dihydrate process.

With the newer dihydrate-hemihydrate process (e.g. PRAYON-CENTRAL GLASS) one get similar by-product conditions as mentioned under 2.1.1.2.

New processes of OCCIDENTAL and FISIONS are producing directly up to 50 %  $P_2O_5$ . Experience for the conversion of this by-product-gypsum is not available.

## 2.1.2 PHOSPHORIC ACID CONCENTRATION PROCESS

(Concentration of acid from 30 to 54 %)

By-product:

fluosilicic acid, 55 kg/t  $P_2O_5$  (as F)

This process is the main source for fluorine for conversion to aluminium fluoride ( $AlF_3$ ), cryolite or fluosilicates.

For the concentration of the acid from a hemihydrate process with about 40 % to 54 % the by-product fluorine will be less, related to the higher initial concentration.

### 2.1.3 SINGLE SUPERPHOSPHATE PROCESS (SSP)

By-product:

fluosilicic acid, approx. 5,5 kg/t SSP (as F)

The Chemie Linz  $AlF_3$ -plant is based on the recovered fluorine from SSP-production.

### 2.1.4 TRIPLE SUPERPHOSPHATE PROCESS (TSP)

By-product:

fluosilicic acid, 0,4 kg/t TSP (as F)

The fluorine recovery is very small and will be only of interest if it will be combined with other fluorine sources of a complex.

There are other process steps where fluorine is evolved but it will be rather difficult or impossible to recover the fluorine.

### 2.1.5 DRYING AND CALCINING OF GYPSUM

No fluorine can be recovered, since the amount of released fluorine is very small related to the off gas.

### 2.1.6 DRYING OF COMPOUND AND COMPLEX FERTILIZERS

Fluorine recovery from the off gas from compound and complex fertilizer production will be impossible due to high dust load and also chemical impurities (e.g. chlorine).

Only the drying stage of fertilizers with a single  $P_2O_5$  component could supply fluorine for a recovery as fluosilicic acid, but care must be taken to find for the recovery economical and physical conditions in respect of temperature and concentration.

The second group of processes are the

## 2.2 GYPSUM ACCEPTING PROCESSES

### 2.2.1 PLASTER, GYPSUM BOARD AND GYPSUM PANELS

Phospho-gypsum for this application should be with low impurities regarding the  $P_2O_5$  and fluorine content. Phosphoric acid and other phosphates cause retardation of early setting and at this time lowers the strenght of the hardened body. Fluorine compounds shorten setting time, and although there is a tendency for lowering the strenght, the effect is small.

Due to that fact phospho-gypsum from hemihydrate-dihydrate process is superior for this application where phospho-gypsum will be obtained with as low as 0,15 %  $P_2O_5$  and 0,18 % fluorine concentration which needs no neutralization.

Phospho-gypsum from dihydrate process needs special treatment (e.g. defluorination by Chemie Linz know-how) repulping and possible neutralization.

There are some processes for reprocessing the phospho-gypsum (GULINI, ICI) which are giving also suitable gypsum for above purposes.

### 2.2.2 GYPSUM FOR RETARD SETTING OF CEMENT

Phospho-gypsum from dihydrate processes is needing special treatment before drying according to ONODA or CHEMIE LINZ know-how, but phospho-gypsum from the hemihydrate-dihydrate process can be used with less difficulty.



### 2.2.3 PRODUCTION OF CEMENT CLINKER AND SULPHURIC ACID, S 5

Production of cement clinker and sulphuric acid based on phospho-gypsum from dihydrate, hemihydrate, dihydrate and dihydrate-hemihydrate (PRAYON/CENTRAL GLASS) phosphoric acid process is solved.

Chemie Linz is operating its sulphuric acid and cement clinker plant, based originally on natural gypsum since 1966 with phospho-gypsum from PRAYON-dihydrate process and a licenced plant is operating at Phalaborwa in South Africa based on phospho-gypsum from PRAYON/CENTRAL GLASS process since 1972 very successfully.

Special know-how allows to lower the  $P_2O_5$  and fluorine content from dihydrate phosphoric acid process down to 0,5 %  $P_2O_5$  and 0,15 % fluorine based on dry dihydrate, which is essential for a proper cement.

Phospho-gypsum from the hemihydrate-dihydrate process with its lower impurity content is used also widely for the production of cement and sulphuric acid.

The co-production of cement clinker and sulphuric acid makes it necessary to evaluate the credit for one of the two products. If you know the credit for the cement clinker you will get the total production cost for the sulphuric acid.

The investment costs are considerable higher than for a single sulphuric acid plant based on brimstone but in spite of that fact CISA/South Africa and Chemie Linz are operating their plants economically successful. With rising brimstone prices this process will gain further importance.

The consumption figures are as follows: see also S 6

Cement from:	Anhydrite	Dihydrate dry or hemihydrate wet (phospho- gypsum)	Dihydrate wet (phospho-gypsum)
Units:	1 t cement + 1 t sulphuric acid		
Raw materials:			
anhydrite or gypsum	kg 1 550	1 950	2 430
coke breeze	kg 95	95	95
clay fly ash or shale	kg 140	140	140
sand	kg 80	80	80
iron oxid	kg 8	8	8
Utilities:			
heat consumption	GJ 6,4	7,8	10
electric energy	kWh 250	250	250
water for cooling	m <sup>3</sup> 45	45	45

By this process you can solve your waste gypsum disposal problem and at the same time you will decrease the dependance of your complex from outside supply.

## 2.2.4 AMMONIUM SULPHATE PROCESS

The well-known ammonium sulphate process (Merseburg process) was modified by Chemie Linz to use phospho-gypsum instead of natural gypsum or anhydrite. The Chemie Linz plant with 180 000 t/a based on natural gypsum was modified in 1967 for use of phospho-gypsum and the process has been licenced already to India and California.

There will be no problem with the phosphor-gypsum from dihydrate and hemihydrate-dihydrate and dihydrate-hemihydrate processes but with phospho-gypsum from hemihydrate processes care has to be taken to avoid filtration problems due to calcium phosphate formation.

The consumption figures are as follows: see also S 7

Raw material:	units		
by-products-gypsum (as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dry)	t/t	1,33 (enters the process filter wet)	
ammonia (100 %)	t/t	0,27	
$\text{CO}_2$ (100 %)	t/t	0,35	
sulphuric acid (100 %)	t/t	0,06	
Utilities:		by-product $\text{CaCO}_3$	
process water	t/t	1,5	1,5
cooling water	t/t	50	50
steam ( 6 bar)	t/t	0,65	0,65
electric power	kWh/t	50	61
instrument air	$\text{Nm}^3/\text{t}$	10	10
fuel	GJ/t	0,32	1,8
Effluent:			
waste water (0,4% $(\text{NH}_4)_2\text{SO}_4$ )	t/t AS	1,5	
By-product: $\text{CaCO}_3$ dry	t/t	0,75	

This by-product calcium carbonate can be further used in the calcium-ammonium nitrate fertilizer production or in the cement production.

Through the conversion of phospho-gypsum to ammonium sulphate one can save the installation of a disposal site and also the solid handling system for the otherwise necessary natural gypsum.

The third group of processes are the

### 2.3 FLUORINE ACCEPTING PROCESSES

#### 2.3.1 PRODUCTION OF ALUMINIUM FLUORIDE

The Chemie Linz aluminium fluoride process based on fluosilicic acid accepts fluorine from various sources within a phosphoric acid and fertilizer complex.

The specification should be as follows:

$H_2SiF_6$	17 - 25 w%
$P_2O_5$	max. 250 mg/l <sup>1)</sup>
$Fe_2O_3$	max. 70 mg/l
Cl	1 g/l <sup>2)</sup>
clear liquid	no suspended matter

- 1) This limit was set to reach only 100 ppm  $P_2O_5$  in the final product what may be actually accepted higher from the side of the aluminium industry. On the other side a new fluorine absorption unit should be designed with minimum possible  $P_2O_5$  level in fluosilicic acid (approx. 50 ppm) to make maximum mother liquor recycle (decrease of consumption figures) possible.
- 2) Higher chlorine contents (up to 20 g/l) are increasing the consumption figures and are influencing the selection of the material for the equipment.

The consumption figures are as follows: see also S 8

Raw materials:	per t $\text{AlF}_3$
aluminium	
hydroxyde (100 %)	1.12 t
$\text{H}_2\text{SiF}_6$ (100 %)	1,10 t
Utilities:	
electrical	
energy	200 kWh
fuel	5 GJ
low pressure	
steam	2 t
cooling water	20 m <sup>3</sup>
scrubber water	max. 50 m <sup>3</sup>
steam condensate	1 m <sup>3</sup>
instrument air	approx. 300 Nm <sup>3</sup>

#### By-products:

Silicic acid may be recycled to the phosphoric acid and the fertilizer complex, for what Chemie Linz may offer also detailed advice for a general improvement.

#### Effluent:

Mother liquor as mentioned before. Recycling to the fluosilicic acid absorption unit will be possible. Otherwise neutralization of the mother liquor is necessary.

Waste water from the scrubber may be used as make up water in the phosphoric acid complex.

### 2.3.2 PRODUCTION OF CRYOLITE

Regarding the fluosilicic acid for the production of cryolite based on the Chemie Linz process the specification will be similar to the one for the production of aluminium fluoride (see 2.3.1).

The consumption figures are as follows: see also S 9

Raw materials:	per t cryolite
aluminium	
hydroxyde (100 %)	0,4 t
fluosilicic	
acid (100 %)	0,75 t
sodium	
carbonate (100 %)	0,85 t
Utilities:	
process water	
(Ca-free)	12 m <sup>3</sup>
cooling water	50 m <sup>3</sup>
steam	3,5 t
electric energy and fuel	a cryolite plant should be normally combined with an aluminium fluoride plant to be more economically

The by-product silicic acid and the waste water may be reused as mentioned before for the aluminium fluoride process.

### 2.3.3 PRODUCTION OF SODIUM FLUOSILICIC AND POTASSIUM FLUOSILICATE

Sodium fluosilicates are often used in water fluoridation (also fluosilicic acid). Processes are available for the production of these fluosilicates and they are also used in the production of opal glass, vitreous enamel, wood preservations, etc.

### 2.3.4 (NEUTRALIZATION OF FLUOSILICIC ACID)

If there is no use for the released fluorine as described in items 2.3.1 to 2.3.3 the fluorine has to be neutralized. As a guide 2,4 kg Ca(OH)<sub>2</sub>/kg F will be necessary for neutralization. This costs should be also credited to the fluorine accepting processes.

The fourth group are the

## 2.4 OTHER PROCESSES WHICH OFFER USEFUL COMBINATIONS WITH ABOVE PROCESSES

### 2.4.1 TAIL GASES FROM MELAMINE PROCESSES

Melamine processes based on urea producing an off gas containing  $\text{NH}_3$  and  $\text{CO}_2$ , which may be separated in its components for further use in the urea plant by the "Chemie Linz off gas treatment process".

If there is in the same chemical complex an ammonium sulphate plant the ammonium carbonate solution which is gained in the off gas treatment process of the melamine process can be utilized directly for the ammonium sulphate production.

From the Chemie Linz melamine process the following amounts of  $\text{NH}_3$  and  $\text{CO}_2$  are recovered:

	per t melamine
$\text{NH}_3$	1,2 t
$\text{CO}_2$	1,1 t

### 2.4.2 OTHER $\text{NH}_3/\text{CO}_2$ TAIL GAS PROCESSES

There are many other processes which are delivering  $\text{NH}_3/\text{CO}_2$  tail gases as

- organic pigment processes based on urea
- production of nuclear fuel
- phenosolvan process
- coal gasification processes

which may be separated by the Chemie Linz/Lurgi process or partly used as feedstock for the preparation of ammonium carbonate solution for the ammonium sulphate process.

### 2.4.3 UREA PROCESS

Off gas from urea plants are containing  $\text{NH}_3$  and  $\text{CO}_2$  which have to be recovered either for the preparation of ammonium carbonate or separated by the Chemie Linz process into  $\text{NH}_3$  and  $\text{CO}_2$ .

### 2.4.4 REUSING $\text{SiO}_2$ FROM $\text{AlF}_3$ AND CRYOLITE PROCESS

The by-product  $\text{SiO}_2$  from  $\text{AlF}_3$  and cryolite processes has a very high activity and can be recycled to the phosphoric acid plant to control the fluorine content of the by-product gypsum.

There are also many other acceptors for silicic acid but they are only interesting under favourable conditions (because of low bulk density and high water content of the silicic acid).

### 2.4.5 REUSING CALCIUM CARBONATE FROM AMMONIUM SULPHATE PRODUCTION

If there is a calcium ammonium nitrate fertilizer production within the fertilizer complex the calcium carbonate from ammonium sulphate production can be used as the calcium component or may be utilized for the cement production.

Slide No. 10 is offering you an interlocking matrix for all the above mentioned processes which may be used as a checklist in finding out possible combinations.



### 3. SOME INTERESTING COMBINATIONS OF ABOVE MENTIONED PROCESSES FOR SOLVING THE POLLUTION PROBLEMS

A chemical complex normally includes a number of above mentioned processes and I would like to show you some interesting combinations with by-product processes.

#### 3.1 STRAIGHTFORWARD CONVERSION OF PHOSPHO-GYPSUM AND EMITTED FLUORINE INTO USEFUL PRODUCTS SHOWN ON A 1 000 t/d $P_2O_5$ DIHYDRATE UNIT WITH A $P_2O_5$ CONCENTRATION TO 54 %

Slide No. 11 details the possible by-product conversion for a 1 000 t/d  $P_2O_5$  plant. The following remarks should be considered to find out whether the conversions are economically sound or not:

- a) For gypsum sulphuric acid plant:  
The credit for the cement!  
Raw material supply for the sulphuric acid production!  
Availability of natural gypsum!
- b) For ammonium sulphate production:  
Ammonium sulphate market (additional supply from processes with by-product ammonium sulphate)!  
Availability of ammonium carbonate solutions within the complex!  
Calcium carbonate demand!
- c) For aluminium fluoride and cryolite production:  
Production of  $AlF_3$  or cryolite of this magnitude will be difficult to market on a free low priced market. Fixed market contracts with the aluminium industry will be necessary (see also cooperation with other industrial complexes par. 4).

### 3.2 ADDITIONAL ADVANTAGES IN COMBINATION WITH PROCESSES DETAILED UNDER 2.4

Slide No. 12 is showing the possible integration of other plants as detailed under item 2.4 and the recycling of converted or recovered by-products.

At first there will be an interesting solution in combining the  $\text{NH}_3/\text{CO}_2$  tail gases of e.g. a melamine and urea plant to recover partly ammonium carbonate in an amount as necessary for the ammonium sulphate production, while the remaining  $\text{NH}_3/\text{CO}_2$  will be separated in a separate step of the particular Chemie Linz process for recycling.

The phospho-gypsum will be used after filtration first for the ammonium sulphate production and the remaining amount after calcination may be combined with natural gypsum to produce the total required sulphuric acid for the whole complex.

### 3.3 CHEMIE LINZ COMPLEX AS AN EXAMPLE

The next slide shows us again the Chemie Linz fertilizer complex.

A chemical complex is normally developing over a number of years and therefore a concept for the integration of future plants is rather difficult.

Chemie Linz started 1954 with a production of sulphuric acid and cement clinker from anhydrite on the basis of an own anhydrite mine. The sulphuric acid was partly used for the production of 280 000 t/a SSP and the rest was sold.

The SSP plant caused soon with the evolved fluorine a severe environmental problem and therefore the own research department got the task to find a process for utilization of the free fluorine.

1963 the Chemie Linz  $\text{AlF}_3$ -plant was taken into service and produced  $\text{AlF}_3$  equivalent to the evolved fluorine of the SSP ( 2 000 t/a  $\text{AlF}_3$ ).

In 1966 a PRAYON phosphoric acid plant of 60 t/d  $\text{P}_2\text{O}_5$  was started. Subsequently the adaption of the gypsum sulphuric acid plant to use phospho-gypsum also as feed stock for the sulphuric acid plant was following.

Alternatively the know-how for the use of the phospho-gypsum for the ammonium sulphate production was developed. This gave to the Chemie Linz complex a considerable flexibility in respect to the rather instable ammonium sulphate market.

The old urea plant delivered first the ammonium carbonate for the  $(\text{NH}_4)_2\text{SO}_4$  production.

The successive installations of melamine 1, 2 and 3 plant (total capacity 35 000 t/a) and the new urea plant (1977) called for the separation of the  $\text{NH}_3/\text{CO}_2$  containing tail gases since ammonium sulphate production was down in these years. Here also flexibility to use cheaper secondary sources at any time is a considerable advantage.

SSP-production dropped by the well known reasons and left the  $\text{AlF}_3$ -plant recently with only sporadic supply of fluosilicic acid. Chemie Linz takes also advantages of this situation and uses now its  $\text{AlF}_3$ -plant to check out the results of the continuous research work in a technical scale. By this way the Chemie Linz  $\text{AlF}_3$  process represents always updated technology. A training program for licencees is offered which gives the opportunity of real trouble shooting.

If a company is considering a grass route fertilizer or phosphoric acid complex or even an expansion of it the engineers responsible for the planning should know about all this possibilities as detailed before to avoid costly investments, which are worthless for later by-product recovery and represent an economical burden which makes it later on difficult to gain the important flexibility.

Chemie Linz is at any time prepared to assist companies in the analysis of complete complexes on the background of its successful experiences.

#### 4. COOPERATION WITH OTHER INDUSTRIAL COMPLEXES

Companies should first investigate their own plant to find out the best possible combinations of existing processes but it will be the task for the company management to gain even more by cooperation with other companies. Following you find described as an example the advantageous for a cooperation between a fertilizer complex and an aluminium smelter complex.

If you are neutralizing the fluorine of a  $P_2O_5$  concentration unit the cost of the neutralization agent should compensate the investment and operating cost for a proper  $H_2SiF_6$  absorption unit which delivers inspect  $H_2SiF_6$  for an  $AlF_3$  plant at zero cost.

Considering the net production cost of a 2 000 t/a  $AlF_3$  plant with zero cost for the  $H_2SiF_6$  you will find, the cost for the aluminium hydroxyde will be as high as 60 % of the net production cost. Together with the problem of floating prices on the free market for aluminium hydroxyde and aluminium fluoride this are the reasons because only few phosphoric acid and fertilizer complexes are going ahead with an  $AlF_3$  project based on  $H_2SiF_6$ .

There will be an entire different situation if you would consider e.g. a joint venture between a phosphoric acid and fertilizer complex and an aluminium smelter complex for the erection of an  $AlF_3$  plant based on  $H_2SiF_6$ .

The Al-smelter company may supply the necessary aluminium hydroxyde from their own production in return for the aluminium fluorine. Cheap bulk transport in the same vessels for the  $Al(OH)_3$  and  $AlF_3$  will be another attractive point.

The two partners can share the investment cost while the smelter complex will only pay the actual production cost plus the profit agreed upon both partners.

The total production cost for a 20 000 t/a  $\text{AlF}_3$  plant will be about 13,5 US cent/kg  $\text{AlF}_3$  (total energy cost + total labour cost + overhead + maintenance cost + 10 % capital depreciation). The cheapest  $\text{AlF}_3$  you can get at the moment on the market will be about 60 US cent/kg exwork.

That leaves enough margin to gain even more than with the route from  $\text{CaF}_2$  to  $\text{AlF}_3$ . Raw materials ( $\text{CaF}_2$ ,  $\text{H}_2\text{SO}_4$ ) are saved and fluorine emission problems are solved on both sides.

This solution should be seriously considered when choosing the route of future  $\text{AlF}_3$ -production.

## ANNEX

- Slide No. 1 World trend in the phosphoric acid production and for the related by-products
- Slide No. 2 Restrictions on fluorine emission and for solid disposals
- Slide No. 3 Chemie Linz Fertilizer Complex
- Slide No. 4 Data on basic processes
- Slide No. 5 Sulphuric acid plant based on phospho-gypsum
- Slide No. 6 Consumption figures for the Chemie Linz gypsum sulphuric acid process
- Slide No. 7 Consumption figures for the Chemie Linz ammonium sulphate process
- Slide No. 8 Consumption figures for the Chemie Linz aluminium fluoride process
- Slide No. 9 Consumption figures for the Chemie Linz cryolite process
- Slide No. 10 Matrix for the interlock of by-product-processes with by-product accepting processes
- Slide No. 11 Straightforward conversion of phospho-gypsum and fluorine into useful products shown on a 1 000 t/d  $P_2O_5$  unit
- Slide No. 12 Scheme for the integration of by-products outside of the phosphoric acid complex
- Slide No. 13 Chemie Linz Fertilizer Complex as slide No. 3

World Trend in the Phosphoric Acid and related By-product Production

Regions	wet Phosphoric Acid Production		By-product Gypsum as 100 % CaSO <sub>4</sub> in 1 000 mt/a <sup>4</sup>	Converted By-products			Total Fluorine 1 000 mt/a	emitted to	converted By-product H <sub>2</sub> SiF <sub>6</sub> or AlF <sub>3</sub>
	1978/79 1) % of 1 000 mt/a total P <sub>2</sub> O <sub>5</sub>	% of expected increases		Cement Clinker	+ H <sub>2</sub> SO <sub>4</sub>	or (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>			
West Europe	4 481	15,6							
East Europe	6 265	21,9	2)						
North America	10 408	36,3							
Latin America	1 279	4,5	2)						
Oceania	196	0,7	2)						
N.W. Africa	1 775	6,2	2)						
Africa except North	934	3,3							
Near East	1 158	4,0	3)						
South Asia	791	2,8	2)						
South East Asia	1 330	4,6							
Socialist Asia	24	0,1							
<b>Total regions</b>	<b>28 641</b>	<b>100</b>		<b>113 295</b>			<b>3 952</b>		
Increase of 10 % of total	2 864			11 329	7 320	7 320	10 800	395	

or → into rivers or the sea  
 → 17,5 km<sup>2</sup> disposal sites

→ recycle to P<sub>2</sub>O<sub>5</sub>-production  
 (80 % of total requirement)

1) Figures from ISMA 1979 Survey

2) about 10 %

3) 20 % or more



Restrictions on fluorine emission and for suspended solid in waste water

Country	waste water limits			fluorine emission to atmosphere		fluorine emission	
	fluorine g/m <sup>3</sup>	kg/t P <sub>2</sub> O <sub>5</sub>	suspended g/m <sup>3</sup>	CaSO <sub>4</sub>	fluorine as gas mg/Nm <sup>3</sup>	total F/t P <sub>2</sub> O <sub>5</sub>	fluorine as gas mg/Nm <sup>3</sup>
USA	15	0,18	1)		1)	10 g	1)
Europe (BRD)	20	1)	30 - 100		20	1)	0,05 HF
USSR	1,5	1)	1,5		1)	1)	0,005
actual	Conventional phosphoric acid plant (54 % P <sub>2</sub> O <sub>5</sub> )	max.470	62	max.30 000	-	300 g	-
	environmentally balanced phosphoric acid plant (54 % P <sub>2</sub> O <sub>5</sub> )	max.20 <sup>2)</sup>	-	max.100 <sup>3)</sup>	<50	18 g	-

1) not available

2) Fluorine is recovered for conversion

3) CaSO<sub>4</sub> is converted or dumped

10 - 24

		<u>Phospho-gypsum</u> in t/t P <sub>2</sub> O <sub>5</sub>		<u>Fluorine as F</u> in kg/t P <sub>2</sub> O <sub>5</sub>
		as dry dihydrate	as dry hemihydrate	
2.1	<u>Basic Processes</u>			
2.1.1	<u>Phosphoric acid processes</u>			
2.1.1.1	Dihydrate process	5		7
2.1.1.2	Hemihydrate-dihydrate process	5		> 7
2.1.1.3	Hemihydrate process Dihydrate - hemihydrate		3,9	> 7
2.1.2	<u>Phosphoric acid concentration process (30 to 54 %)</u>			55
2.1.3	<u>SSP</u>			5,5 kg/t SSP
2.1.4	<u>TSP</u>			4 kg/t TSP

Consumption figures for the CHEMIE LINZ GYPSUM SULPHURIC ACID PROCESS

<u>Cement from</u>		Anhydrite	Dihydrate dry or hemihydrate wet (phospho-gypsum)	Dihydrate wet (phospho-gypsum)
<u>Units:</u>		1 t cement	+ 1 t	1 t sulphuric acid
<u>Raw materials:</u>				
anhydrite or gypsum	kg	1 550	1 950	2 430
coke breeze	kg	95	95	95
clay, fly ash or shale	kg	140	140	140
sand	kg	80	80	80
iron oxid	kg	8	8	8
<u>Utilities:</u>				
heat consumption	GJ	6,4	7,8	10
electric energy	kWh	250	250	250
water for cooling	m <sup>3</sup>	45	45	45

10 - 26

Consumption figures for the CHEMIE LINZ AMMONIUM SULPHATE PROCESS

<u>Raw materials:</u>	<u>units</u>	
by-product-gypsum (as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dry)	t/t	1,33 (enters the process filter wet)
ammonia (100 %)	t/t	0,27
$\text{CO}_2$ (100 %)	t/t	0,35
sulphuric acid (100 %)	t/t	0,06

<u>Utilities:</u>		by-product $\text{CaCO}_3$	
		wet	dry
process water	t/t	1,5	1,5
cooling water	t/t	50	50
steam ( 6 bar)	t/t	0,65	0,65
electric power	kWh/t	50	50
instrument air	$\text{Nm}^3/\text{t}$	10	10
fuel	GJ/t	0,32	1,8

Effluent:

waste water (0,4 % $(\text{NH}_4)_2\text{SO}_4$ )	t/t AS	1,5
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By-product:

$\text{CaCO}_3$ dry	t/t	0,75
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10 - 27

Consumption figures for the CHEMIE LINZ ALUMINIUM FLUORIDE PROCESS

Raw materials:

	<u>per t AlF<sub>3</sub></u>
aluminium hydroxyde (100 %)	1,12 t
H <sub>2</sub> SiF <sub>6</sub> (100 %)	1,10 t

Utilities:

electric energy	200 kWh
fuel	5 GJ
low pressure steam	2 t
cooling water	20 m <sup>3</sup>
scrubber water	max. 50 m <sup>3</sup>
steam condensate	1 m <sup>3</sup>
instrument air	approx. 300 Nm <sup>3</sup>

Consumption figures for the CHEMIE LINZ CRYOLITE PROCESS

Raw materials:

per t cryolite

aluminium hydroxyde (100 %)	0,4 t
fluosilicic acid (100 %)	0,75 t
sodium carbonate (100 %)	0,85 t

Utilities:

process water (Ca-free)	11 m <sup>3</sup>
cooling water	max. 115 m <sup>3</sup>
steam	max. 5,3 t

electrical energy  
fuel

a cryolite plant should be normally combined with a aluminium fluoride plant to be more economically.

Matrix for the interlock of processes with by-products with by-products accepting processes

Processes with by-products	By-products	By-product accepting processes												
	emission	disposal	2.2.1	2.2.2	2.2.3	2.2.4	2.3.1	2.3.2	2.3.3	2.4.3	2.4.5			
	CaSO <sub>4</sub> Fluorine SiO <sub>2</sub> NH <sub>3</sub> /CO <sub>2</sub> CaCO <sub>2</sub>	CaSO <sub>4</sub> CaF <sub>2</sub> (Neutralization)	Plaster Gypsum board Gypsum panels	Gypsum for re- tard setting of cement	H <sub>2</sub> SO <sub>4</sub> Cement	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	AlF <sub>3</sub>	Cryolite	Fluosilicates	Urea plant	Calcium Ammonium nitrate or cement	H <sub>2</sub> SiF <sub>6</sub> Absorption	P <sub>2</sub> O <sub>5</sub> Production	
2.1.1.1 Dihydrate process	●	●	●	●	●	●	●	●	●			●		
2.1.1.2 Hemihydrate-dihydrate process	●	●	●	●	●	●	●	●	●			●		
2.1.1.3 Hemihydrate process	●	●					●	●	●			●		
2.1.2 Phosphoric acid concentration process	●	●						●	●			●		
2.1.3 SSP	●	●						●	●			●		
2.1.4 TSP	●	●						●	●			●		
2.1.5 Drying and calcining of gypsum	●	●												
2.1.6 Drying of compound and complex fertilizer	●	●												
2.4.1 Tail gases from melamine processes							●			●				
2.4.2 Other NH <sub>3</sub> /CO <sub>2</sub> tail gas processes							●			●				
2.4.3 Urea processes							●			●				
2.4.4 AlF <sub>3</sub> and cryolite	●	●										●	●	
2.4.5 Ammonium sulphate process											●			
2.3.4 Neutralization of fluorine		●												
Chemie Linz NH <sub>3</sub> /CO <sub>2</sub> separation process							●			●				

10 - 30

Straightforward conversion of phospho-gypsum and fluorine into useful products shown on a unit of  
1 000 t/d P<sub>2</sub>O<sub>5</sub> from dihydrate process inclusive concentration unit (30 % - 54 %) all figures in t/d

By-product conversion:

	H <sub>2</sub> SO <sub>4</sub>	Cement-clinker	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SiF <sub>6</sub> (100 %)	AlF <sub>3</sub>	Cryolite
<u>By-products:</u>						
CaSO <sub>4</sub> x 2H <sub>2</sub> O dry	5 000	2 564	2 564	(3 760)		
Fluorine from attack section	7					
Fluorine from concentration section	55					
combined	62			78	71	(104)

Necessary raw materials:

H <sub>2</sub> SO <sub>4</sub> (100 %)	3 000 =	436	+	2 564		
Al(OH) <sub>3</sub> (100 %)		80				
		42				
Na <sub>2</sub> CO <sub>3</sub> (100 %)		88				

Production	2 564	(3 760)	71	(104)
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Aluminium melting unit	1 000 t/d			
aluminium fluoride	consumption		30	
cryolite	approx.			20

(alternatively)

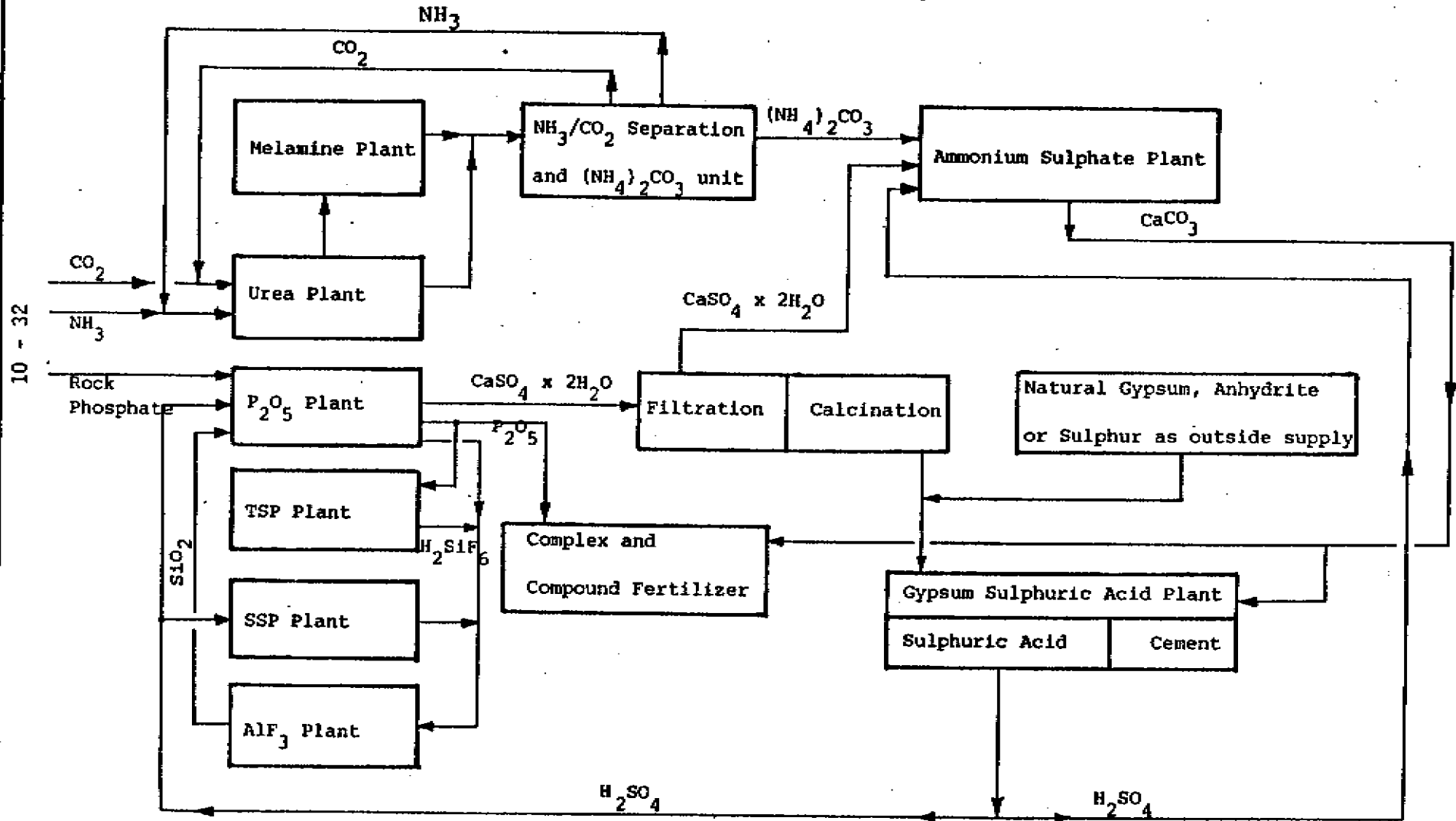
outside supply

CHEMIE LINZ AG

S 11  
1979



Scheme for the Integration of By-products outside of the  
Phosphoric Acid Complex



10 - 32

A/80/10 Environmentally and economically balanced phosphoric acid and fertilizer complexes by H.D. Schneider, Chemie Linz AG, Austria.

DISCUSSION : (Rapporteur B. Neveu, APC, France)

Q - Mr. V. VANECEK, RIIC, Czechoslovakia

- 1) What is the quality of the clinker from the production of cement and  $H_2SO_4$ , when phospho-gypsum of different quality is used?
- 2) At Linz, is phospho-gypsum solely used or a mixture with natural anhydrite?
- 3) What is the approximate production capacity at Linz?

A -

- 1) There is no quality problem with a phospho-gypsum of 0.5%  $P_2O_5$  or less and of 0.15% F or less, even if there are variations of the impurities within these limits. With phospho-gypsum exceeding these limits, one can observe with increasing  $P_2O_5$ -content a loss of the early setting strength and with increasing fluorine content rings may be observed in the cement kiln and the retard setting of the cement is getting unstable.
- 2) Chemie Linz is using in its gypsum sulphuric acid plant either natural anhydrite or phospho-gypsum and also mixtures of both raw materials, whatever is necessary to balance the by-product phosphogypsum amount between the cement plant and the ammonium sulphate plant.
- 3) The Chemie Linz production is 240 t/d clinker.

Q - Mr. P. MORAILLON, Générale des Engrais, France

- 1) In the case of triple superphosphate manufacture, with a low fluorine recovery, is the figure of 4 kg F/t TSP mentioned in the text correct?
- 2) In aluminium fluoride manufacture are the consumption figures indicated, which correspond to 80% F recovery, obtained with or without recycling of mother liquors to the absorption of fluosilicic acid?

A -

- 1) Please correct (2.1.4 on 10-6 and 10-25): "fluosilicic acid: less than 0.4 kg/t TSP (as F)".
- 2) The fluorine conversion of 78% corresponding to the stated consumption figures does not take into account a possible recycling of mother liquor to the absorption unit.

Q - Mr. M. BONGARD, Windmill Holland, Netherlands

In a sulphuric acid plant based on gypsum where are the impurities of the gypsum going?

For example will cadmium of gypsum go into the air with off-gas?

A - The impurities of the phospho-gypsum are found mainly in the cement clinker. There is no risk of cadmium leaving into the air with off-gases.

Q - Mr. M. BARLOY, CERMI, France

What should be the price of sulphur so that the production of sulphuric acid and clinker from gypsum is economic?

A - Economic production of sulphuric acid and cement clinker by phospho-gypsum in competition with sulphur price.

1 000 t/d H<sub>2</sub>SO<sub>4</sub> from phospho-gypsum  
1 000 t/d cement clinker from phospho-gypsum

Plant location at Chemie Linz plant site  
Calculation based on 1980 raw materials and utilities cost.

	AS/to H <sub>2</sub> SO <sub>4</sub>
raw materials .....	130
(fly ash, coke breeze, sand)	
utilities cost .....	630
(cooling water, steam, electrical energy, cunker oil, plant air)	
capacity - variable cost .....	708
(operators, maintenance, overheads, laboratory, depreciation, capital interest, taxes and insurance)	
Bonus for otherwise necessary deposit of gypsum	1 468
Bonus for cement	- 243
Coproduct price	- 502
	AS/to H <sub>2</sub> SO <sub>4</sub> 723

This price is corresponding to a sulphur price of "1 880 AS/to S".

Q - Mr. R. VAN HARDEVELD, D.S.M., Netherlands

The reuse of calcium carbonate from ammonium sulphate production in calcium ammonium nitrate (C.A.N.) fertiliser is indicated. Have you any experience with this process and if so is the activity of the precipitated calcium carbonate low enough to prevent serious calcium nitrate formation which will induce product quality problems?

A - Based on our experience of many years reusing calcium carbonate from our AS-production for CAN-granulation (screw and drum) we produce CAN with no problems in product quality.

Due to ASU production capacity, we mix by-product calcium carbonate and limestone, but even 1:1 mixtures do not cause problems in product quality by too high Ca(NO<sub>3</sub>)<sub>2</sub>-formation.

Q - Mr. A. DAVISTER, Soci t  de Prayon, Belgium

I would like to make an important remark concerning the information given on pages 4 and 5. Indeed phospho-gypsum from industrial plants based on the hemihydrate-dihydrate process can never be used as such to make plaster. We process 250,000 t/yr and I can assure you that it must be purified just as gypsum from dihydrate monocrystal processes in order to remove soluble salts, acidity and other noxious substances. Can you comment?

A - As you comment soluble salts and the acidity (pH) of the phospho-gypsum will be an important measure for direct use of phospho-gypsum in the production of plaster walls, but these parameters are mainly depending on the actual design (reserves) of the gypsum filter and therefore the answer should be given by the process licensor or the engineering company which has done the actual design of a particular plant.

Q - Mr. H.T. KAPADIA, Dharamsi Morarji Chemical Co. Ltd, India

- 1) Do you observe silica deposits in the fluorine scrubbers of super-phosphate and phosphoric acid? If so, what steps would you suggest to take to avoid silica in  $H_2SiF_6$  solution, which causes problems such as clogging of nozzles and poor absorption efficiency, etc...
- 2) What is the reason for specifying calcium free process water for cryolite manufacture?

A - 1) Precipitated  $SiO_2$  in the scrubbers of the  $H_2SiF_6$  absorption unit of our SSP-plant settles on the bottom of the scrubbers and gets removed from there from time to time. The amount of precipitated  $SiO_2$  in SSP-production depends on the ratio of the evolved  $SiF_4$  and HF. It could be only influenced by addition of HF. Chemie Linz has no  $P_2O_5$ -concentration unit. We observe only  $Na_2SiF_6$  deposits in the evaporation coolers which are removed from time to time, but there is no plugging of nozzles.

2) The dilution of the  $AlF_3$ -solution with Ca-containing process water would result in the precipitation of  $CaF_2$ , which would be found in the final product.

Q - Mr. V.V. RAO, Dharamsi Morarji Chemical Co. Ltd., India

- 1) You have stated that a cryolite plant should normally be combined with an aluminium fluoride plant. Do the raw materials and utilities consumptions (electrical energy and fuel consumption have not been given in the table) stated on p. 13 refer to a cryolite plant combined with an  $AlF_3$  plant? If the cryolite plant is to be operated independently, what will be the raw materials and utilities required, including energy and fuel?
- 2) Frequently, 17%  $H_2SiF_6$  available from phosphoric acid plants contains very high  $P_2O_5$ , about 600-1000 ppm. What treatment would you advise to reduce this to 250 ppm  $P_2O_5$  as specified in 2.3.1. of your paper?

- A -
- 1) For the cryolite production, one needs according to the Chemie Linz process diluted aluminium fluoride and sodium fluoride solution. In the case of a combined  $AlF_3$ /cryolite plant, there is the possibility of a joint preparation of the  $AlF_3$ -solution and also joint use of parts of the calcination. This means that the investment costs are lower than for single plants, but the raw material consumptions will be the same as for single plants as also stated in the paper. Only the utilities consumption will be less than the addition of the figures of single plants, but the exact value depends on the ratio between  $AlF_3$  and cryolite production.
  - 2) The main concern of every chemical complex should be to observe during the design stage of a phosphoric acid complex already all aspects of later by-product utilization (e.g. evaporator design, space site for absorption units, absorption system, etc...). To reduce the  $P_2O_5$  level in the  $H_2SiF_6$  of an existing plant the installation of a special separator (e.g. from Lurgi) has to be taken into consideration. Properly designed plants produce easily  $H_2SiF_6$  with less than 50 ppm, which allows a high percentage of recirculation of the mother liquor from the  $AlF_3$ -plant.
  - 3) 0.15 w %  $SiO_2$  max. for  $AlF_3$  ) expected figures  
0.3 w %  $SiO_2$  for cryolite )

Q - Mr. B. NEVEU, APC, France

At identical production capacities of finished products (clinker and sulphuric acid) how can you compare the investment costs and the heat balance of a mixed sulphuric acid and cement production complex according to the Linz process to those of a sulphuric acid plant using sulphur and to a conventional cement unit based on dry process?

A - Comparison of a conventional cement and sulphuric acid plant with a gypsum sulphuric acid plant

	Investment Million \$	Thermal energy requirements GJ per 1 t cement clinker and 1 t $H_2SO_4$
500 t/d $H_2SO_4$ from brimstone ) 500 t/d cement clinker from $CaCO_3$ )	50	+ 0.4
500 t/d $H_2SO_4$ ) 500 t/d cement clinker) based on phosphogypsum (wet dihydrate)	70	- 10

+ excess  
- consumption