

# **IFA Technical Conference**

Venice, Italy 2-4 October 1990

## ENVIRONMENTAL IMPROVEMENTS AND ENERGY SAVINGS IN THE HYDRO SUPRA PHOSPHORIC ACID PLANT

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#### SUMMARY

In 1963-67 Supra AB installed a Dorrco (Jacobs) dihydrate phosphoric acid plant at their production site in Landskrona, Sweden. By the 1980's the increase in energy and raw material prices motivated the company to investigate ways of achieving production cost savings.

A feasibility study was undertaken to examine the costs and benefits of converting the phosphoric acid plant to the Hydro HDH process. Details of the study given in this paper showed that a considerable cost saving could be achieved with the HDH route.

The plant was therefore converted to the HDH process during 1987. During the project top priority was given to reducing effluent discharges. By using a closed loop water recirculation system, the plant is a liquid effluent free unit. The reduction in the requirements for process and cooling water of the HDH process has improved the water management system.

Supra also installed a comprehensive fluorine scrubbing system which not only reduces gaseous fluorine emissions to 5 mgF/m<sup>3</sup> but also produces by-product fluosilicic acid (up to 25%  $\rm H_2SiF_6$ ) with negligible  $\rm P_2O_5$  contamination which is sold to a nearby  $\rm AlF_3$  manufacturer.

The conversion to the HDH process resulted in an increase in  $P_2O_5$  recovery efficiency from 96% to more than 98%. The energy savings were also substantial. In the production of NPK fertilizers the overall saving is approximately 900 kWh/t  $P_2O_5$ .

#### INTRODUCTION

In the fertilizer plant at Landskrona, Hydro Supra produces superphosphate, phosphoric acid and nitric acid as intermediates and CAN, GTSP, PKs and NPKs as final products. Attached flow sheet shows the material balance. No sulphuric acid is produced on the site.

The phosphoric acid plant was until 1987 a DH plant with a yearly capacity of 70,000 tons  $P_2O_5/\text{year}$ . The nominal capacity was 50,000 tons  $P_2O_5/\text{year}$  and the plant operated on blends of Florida (70/72% BPL) and Khouribga K11 rocks.

35,000 tons  $P_2O_5$  was concentrated to 52-54%  $P_2O_5$  in a flue gas phosphoric acid evaporator treated by natural gas. The process was liscensed by Agrimont. For details of the fluorine recovery system see  $^{(1)}$ .

No fluorine recovery was installed in the phosphoric acid reaction section. The reactors were two air-cooled single tank reactors in parallel designed by Dorr-Oliver (Jacobs).

The filter section consisted of three 15 m2 Landskrona belt filters.

The  $P_2O_5$ -efficiency on a yearly balance was 96%. The  $P_2O_5$  emissions were very low due to the closed water system to the gypsum island <sup>(2)</sup>.

The energy balance of the Landskrona plants was deficit due to the fact that no sulphuric acid is produced.

It was obvious that a major reduction in production costs could be achieved by reducing energy usage. As the NPK plant in Landskrona operates on  $42 \text{ P}_2\text{O}_5$ , the HDH-process was studied as a means to reduce energy costs and improve  $\text{P}_2\text{O}_5$  recovery.

For details of the HDH process see (3), (4) and (5).

#### 1. PROJECT DETAILS

The project began with the evaluation of the costs and benefits of a number of options. Each option was based on the conversion of the existing dihydrate phosphoric acid plant to the HDH process. The main variable in each case was the plant production rate and this was dictated by which items of existing equipment should be used and which should be replaced.

#### 1.1 <u>Design Basis</u>

Phosphate Rock Source: Florida 70/72 BPL; Khouribga 70 BPL

Sulphuric Acid Feed:

Concentration: 98%

Expected P<sub>2</sub>O<sub>5</sub> Efficiency: 98,5% (based on dihydrate

cake losses)

Maximum Permitted

Gaseous Effluent: 0.02 kg F/tonne P<sub>2</sub>0<sub>5</sub> produced

Maximum Permitted

Liquid Effluent: 5 kg P<sub>2</sub>0<sub>5</sub>/day

The use of reclaimed gypsum slurry water with a chloride content of 540 ppm has also been assumed.

#### 1.2 Options Considered

- 1. Conversion to HDH process at a rate of 270 tpd  $P_2O_5$  (equivalent 84,000 tpa  $P_2O_5$ ).
- 2. Conversion to HDH process at a rate of 320 tpd  $P_2O_5$  (equivalent 100,000 tpa  $P_2O_5$ ).
- 3. Conversion to HDH process at a rate of 360 tpd  $P_2O_5$  (equivalent 111,600 tpa  $P_2O_5$ ).

To summarise the reasons for the selection of each option:

#### Option 1

The existing plant contains three off 15  $\rm m^2$  Nordingren belt filters. This combined filter area of 45  $\rm m^2$  corresponds to the required hemihydrate filter capacity for 270 tpd  $\rm P_2O_5$  output.

#### Option 2

Corresponds to the output rate, indicated by Supra, as that most suited to their immediate production requirements.

#### Option 3

Corresponds to a rate where the existing filters are matched to the dihydrate filter area requirement.

There are two cases: firstly when the existing filters plus one new 15  $\text{m}^2$  belt filter are used for hemihydrate filtration and a new 45  $\text{m}^2$  filter is used for dihydrate filtration (3A). Alternatively, a new 60  $\text{m}^2$  belt filter is used for hemihydrate filtration and the existing (3 x 15  $\text{m}^2$ ) filters are used for dihydrate filtration (3B).

The filtration and reaction requirements are tabulated below.

Option 3B Option 1 Option 2 Option 3A 360 360 Production Rate 270 320 tpd Poc m<sup>3</sup> Reactor 1A 105 (E) 105 (E) 105 (E) 105 (E) m<sup>3</sup> Reactor 1B 234 (N) 234 (N) 199 (N) 152 (N) m<sup>3</sup> 170 (E) 170 (E) Reactor 2 170 (E) 170 (E) 22 (E) 22 (E) Filter Feed Tank 22 (E) 22 (E) 45(E)+10(N) 45(E) + 15(N) 60 (N) **Hemihydrate** 3x15 (E) Filter Area m<sup>2</sup> 540 (N) 540 (N) Transformation 405 (N) 480 (E) Tank Dihydrate Filter 45 (N) 3x15 (E) 34 (N) 40 (N) Area

Table 1

Note (E) = Denotes the use of existing equipment.

(N) = Denotes the use of the new equipment.

Both air cooling and flash cooling were considered for all four options.

#### 1.3 Outcome of the Study

The returns on investment show the 360 tpd  $P_2O_5$  options to be the most attractive. The difference in cost between options 3A and 3B were within estimating accuracy. However, process and plant layout considerations marginally favour option 3B for the following reasons:

- (a) Materials of construction of the existing filter equipment is more suited to the dihydrate duty.
- (b) Easier gypsum disposal.

The evaluation of flash versus air cooling, show the former to be less expensive. Process experience of both types of cooling systems strongly favour the use of flash cooling.

Therefore option 3B utilising flash cooling was selected. However, there was one additional change required. When the existing reactors were inspected in detail they were found to be non-serviceable and in need of replacement regardless of the process route to be used. So in any event the reactors would have to be replaced.

#### 1.4 Special Conditions

There are very strict effluent regulations in Sweden so it was necessary to ensure effluent discharge was minimised. Therefore for gypsum disposal Hydro Supra utilised its pond system on the island in the Sound. However, the process water return from the island is contaminated with a relatively high level of chloride so materials of construction for items of equipment such as agitators, pumps etc, had to be selected to withstand the corrosivity of the chloride. Typically stainless steels such as Sanrico 28 or rubber covered mild steel were used.

The need to reduce gaseous fluorine emissions led to the installation of fluorine scrubbing system on the reaction system and flash cooler. Because Supra has a market for 20-25%  $H_2SiF_6$  with a negligible  $P_2O_5$  content the fluorine recovery system was designed specifically to achieve this product (see Section 2.1).

#### 2. <u>ENVIRONMENTAL IMPROVEMENTS</u>

#### 2.1 Fluorine Recovery

In the HDH-plant a fluorine recovery was installed in the reactor section. Fluosilicic acid of 20-25%  $H_2SiF_6$  and with a  $P_2O_5$  content lower than 100 ppm was needed for AlF<sub>3</sub> production.

Hydro Supra had developed a process that had been in successful operation in the superphosphate plant since 1978 (see Figure ).

The gases from the flash cooler or the reactors first go to a venturi section and then to a droplet separator. The scrubber liquor is a high strength fluosilicic acid solution.

Any phosphate entrained in the gas stream is removed. The scrubber liquor is an azeotropic solution and therefore absorbs only a small amount of fluorine.

The gases then pass two cyclonic scrubbers where the fluosilicic acid is recovered before the final droplet separator. The acid concentration is 20-25%  $H_2SiF_6$  and the fluorine emission is 5-10 mg  $F/m^3$ .

The fluorine recovery is designed to avoid additional down-time in the phosphoric acid plant due to blockage of pipes and gas ducts

The fluosilicic acid is aged and filtered on a semi-continuous belt filter to produce a clear solution.

#### 2.2 Gypsum disposal

The gypsum disposal has been described in detail at the IFA technical conference in Greece 1982.

The water system is closed and thus the pond water is used for washing the DH filter cake. However, a final wash of fresh water has been found to be economical.

#### PLANT PERFORMANCE

#### 3.1 Plant Start-up and Operation

The revamped plant very soon operated at and above designed capacity, but the on-stream factor was too low. Scaling around the filters were the main source of problems.

Scaling around the HH filter was found to be caused by the formation of calcium sulphate anhydrite. However, changes to the sulphuric acid feed system to the reactors gave an immediate improvement in operations. The HH filtration now operates very well.

The other problem occurred when using 100% Florida rock, when the transformation from HH to DH was incomplete. The disadvantage was not so much the P<sub>2</sub>O<sub>5</sub> recovery as in the transformation of HH to DH in the filter pipe-work which resulted in scaling problems. In order to increase the rate of transformation of HH to DH, active silica was added to the transformation tank whenever 100% Florida rock was fed to the plant. This has solved the problem and stable operation of the DH filters is now maintained.

The transformation of HH to DH when using Khouribga rock or blends of Khouribga and Florida rock is satisfactory, without the use of additives.

With the above modifications the plant now operates above design capacity.

During normal operations with these rocks the  $P_2O_5$  recovery efficiency is in excess of 98% due to the benefits of the HDH process and the recycle of pond water.

A typical analysis of the product acid is:

41-42% P<sub>2</sub>O<sub>5</sub>

2% H<sub>2</sub>SO<sub>4</sub>

0,9% F

0,06% C1

0,2-0,3% Si

1,5% solids ex plant

 $^{30}~\rm kg~H_2SiF_6/tonne~P_2O_5$  is produced in the HDH section. The fluosilicic acid from the evaporator is recycled to the superphosphate plant.

#### 3.2 Energy Balance

Another major benefit of the HDH process is the energy economy. Two typical balances for Hydro Supra are as follows.

## 3.2.1 The NPK plant operates on 42 P<sub>2</sub>O<sub>5</sub>.

DH-process. kWh/t (42% P20g)

	Grinding	Phos.acid plant	Evaporation	Total
Electricity	60	100	80	240
Gas	-	-	960	<u>960</u>
				1200

### HDH-process kWh/t (42% P2O5)

	Grinding	Phos.acid plant	Evaporation	Total
Electricity	-	180	_	180
Steam	_	60		<u>60</u>
		·		240 ===

3.2.2 Phosphoric acid is also used for run-of-pile TSP and export within the company. An energy balance for 52% P<sub>2</sub>Q<sub>5</sub> acid is as follows in Hydro Supra's case:

DH-process. kWh/t (52% P2O5)

	Grinding	Phos.acid plant	Evaporation	Total
Electricity	60	100	100	260
Gas	<b>–</b>	<del>-</del>	1440	1440
				1700 ====

HDH-process kWh/t (52% P205)

	Grinding	Phos.acid plant	Evaporation	Total
Electricity	_	180	40	220
Steam	-	80	80	160
Gas	_	-	500	500
				880 ===

The energy savings are considerable. No rock is ground, but the major savings are in reduced energy need for evaporation. The capacity of the evaporator has increased from 30 K tonnes/year to 75 K tonnes/year.

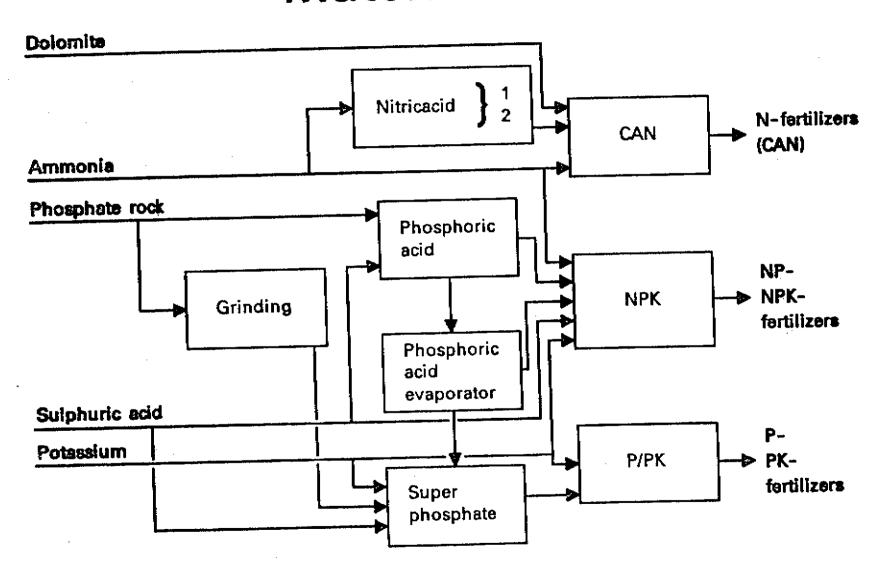
#### 4. FURTHER WORK

A pilot plant for further improvement of the Norsk Hydro process has been erected in Landskrona. A mobile pilot plant for Cadmium extraction has already been in operation for some years.

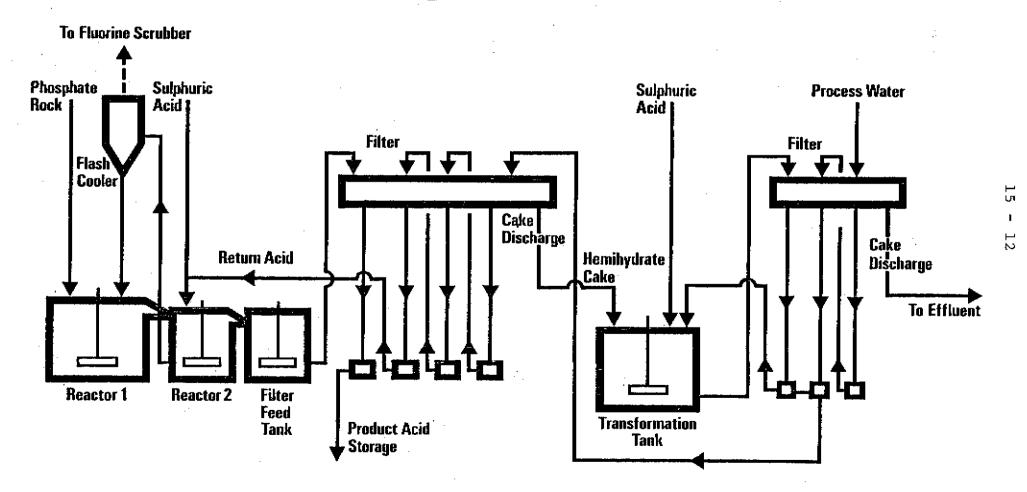
#### REFERENCES

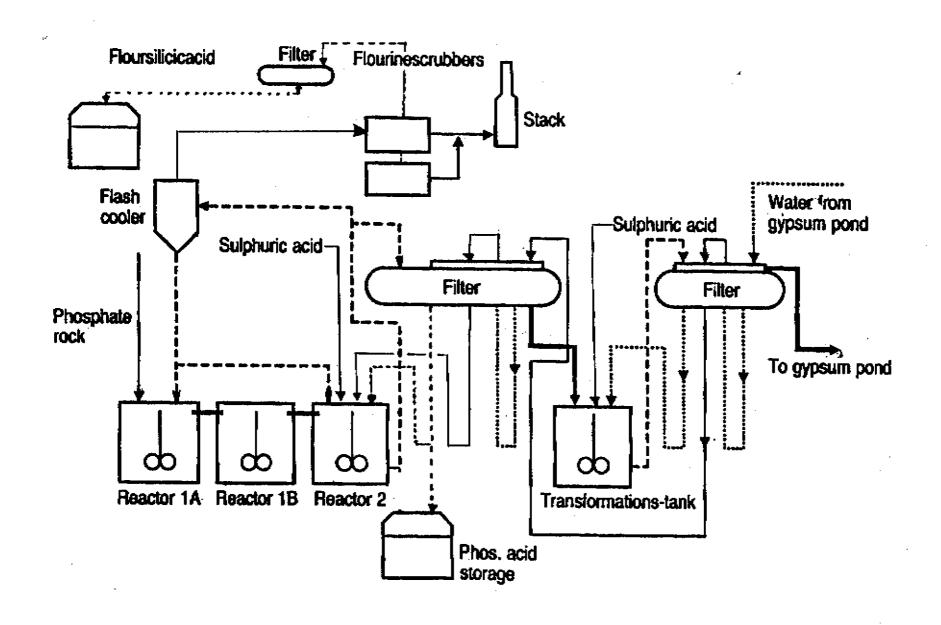
Paper	Author(s)	Presented to
(1) Investigation of an aerosol with pilot units installed on site	G. Modig	IFA, The Hague, Netherlands, 1976
<sup>(2)</sup> Gypsum Island in the Sound	G. Wiberg	IFA, Kallithea, Greece, 1982
<sup>(3)</sup> The Case for Hemihydrate	B.T. Crozier	Agrichem'88, Nitra Czechoslovakia,1988
(4) Hemihydrate Performance of Florida Rock in a Converted Phosphoric Acid Plant	N. Kolmeijer	Fertilizer Industry Round Table, Atlanta, Georgia, USA, 1985
(5) Hemihydrate Operating Experience at Brunswick Mining and Smelting Fertilizer Facilities	T. Gravestock	IFA, Edmonton, Canada, 1988

# **Material Flow**



# **Hemidihydrate Process**





## FLUORINE RECOVERY

