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# NON-CONVENTIONAL FERTILIZER RAW MATERIALS AND PROCESSES

N. Louizos  
The Hellenic Chemical Products & Fertilizers Co., Greece

## 1. INTRODUCTION

The cost of production of fertilizers depends mainly on raw materials, economy of scale and innovation. Greece is a small country with relatively small fertilizer market and having almost no indigenous raw materials (apart from pyrites and recovered sulphur). Therefore it depends heavily on innovation.

In order to minimize the production cost of fertilizers, The Hellenic Chemical Products and Fertilizers Co. has encouraged the use of non-conventional fertilizer raw materials and processes.

Non-conventional raw materials include by-products of activities outside the fertilizer industry, which however contain useful elements for fertilizer production. This is exactly what the ecologists might call recycling of useful raw materials.

Non-conventional processes are simple innovative features which fit to specific pieces of installation in order to increase their utilization, flexibility and productivity. These include either chemical or physical processes.

## 2. THE HELLENIC CHEMICAL PRODUCTS & FERTILIZERS CO.

The Hellenic Chemical Products & Fertilizers Co (HCPF) founded in 1909 is the oldest fertilizer company in Greece, with its main activities in the mining and chemical sector including fertilizers, acids, pesticides, flat glass and chemical products, as well as lead and zinc sulphides and pyrites.

The main production complex is situated at the entrance of the port of Piraeus which is part of the greater Athens area.

As it is shown in Figure 1, this complex comprises the following plants:

- 400 tpd sulphuric acid plant (No 3) which is a single absorption plant based on sulphur.
- 700 tpd sulphuric acid plant (No 4) which is a double absorption plant of mixed type i.e. based on sulphur and pyrites.
- 800 tpd-SSP/TSP-plant based on a Broadfield-den.
- Two conventional NPK slurry granulation plants with capacities of 1200 tpd (No 4) and 800 tpd (No 5) respectively.
- 400 tpd compaction granulation plant using exclusively solid raw materials.

The main fertilizer grades produced are 16-20-0, 20-10-0, 11-15-15, 0-20-0 (SSP), 24-12-0, 14-14-14 etc. The production of the above plants serves about 25% of the Greek market which is of the order of 2 million tonnes per year, while a small portion of it is also exported.

### 3. THE USE OF VINASSE IN FERTILIZER PRODUCTION

Vinasse is the distillery effluent from the production of ethanol from mollasse which in turn is a by-product of sugar industry.

A typical analysis of vinasse is:

pH		: 4 - 4.5
BOD <sub>5</sub>	(mg/l)	: 27500 ± 9500
COD	(mg/l)	: 65500 ± 25000
Total N	(mg/l)	: 750 ± 150
Total P <sub>2</sub> O <sub>5</sub>	(mg/l)	: 100 ± 50
Total K <sub>2</sub> O	(mg/l)	: 6700 ± 3500

Taking into account the existing effluent treatment technologies vinasse is considered to be among the most difficult effluents to treat due to its high BOD and COD values. On the other hand, as it contains useful fertilizer elements that can be used as a fertilizer material provided it is incorporated in to conventional fertilizers.

The first problem to overcome is that it is a very dilute solution which is difficult and costly to transport and mix with other fertilizer materials. For this reason, before transportation it is condensed to a solution of the following analysis:

% N	: 3
% P <sub>2</sub> O <sub>5</sub>	: 0.2
% K <sub>2</sub> O	: 6
% Solids	: 60

The second step is to incorporate the above liquid (slurry) in the fertilizer process. From the various options available it was decided to add vinasse in the reaction step so that to exploit the heat of reaction to remove part of its water content. The resulting slurry is subsequently processed as usual in the granulator etc. From the production point of view no significant problem was observed using vinasse in the production of NPK fertilizers, apart from the characteristic strong odor of the organic material.

The rate at which vinasse is added to the fertilizer is ca 50 kg vinasse/ton of final product, the limiting factors being the problems of odor and frothing in the reactor.

The third problem to be checked was the efficiency of the N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O content of vinasse from the agronomical point of view i.e. if the above elements in the form they are present in vinasse are equivalent in nutrient value as the normal fertilizer components.

Several pot-scale experiments were performed in a special greenhouse on several plants.

The results of these experiments show that:

- the nitrogen of the vinasse which is mainly in organic form is available to the plants only after a few weeks
- on the contrary the potassium contained in vinasse is completely water soluble and therefore has the same nutrient value as K<sub>2</sub>SO<sub>4</sub>.

The potassium uptake by the plant was found slightly higher in the case of vinasse than in the case of K<sub>2</sub>SO<sub>4</sub> possibly due to the organic material as well as other micronutrients contained in vinasse.

#### 4. RECYCLING BY-PRODUCTS OF DETERGENT AND EXPLOSIVES INDUSTRY INTO FERTILISER PRODUCTION

Significant amounts of sulfuric acid are used by the detergent industry whereby the process creates effluent sulfuric acid contaminated by organic material. Similarly production of nitroglycerine is creating effluent sulfuric acid contaminated by nitric acid. These two streams of effluents are difficult or costly to treat individually. In order to help its sulfuric acid customers to overcome the problem of treating these effluents, HCPF is taking back these effluents, which after mixing give a 75% sulfuric acid solution (whereby the organic material is oxidised by nitric acid) and can be recycled either in the production of SSP or in the production of phosphoric acid.

#### 5. SUBSTITUTION OF SULFURIC ACID BY HYDROCHLORIC ACID IN SSP PRODUCTION

HCPF is producing hydrochloric acid as a by-product in the production of  $K_2SO_4$  in the Mannheim furnace process. Since the main product is much cheaper than the imported one, the production rate is kept at the maximum.

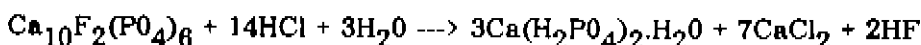
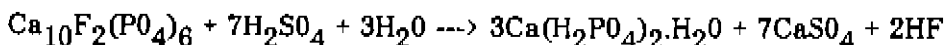
As the market for hydrochloric acid is fluctuating it becomes sometimes difficult to sell at any one time all the HCl produced.

To solve this problem the use of hydrochloric acid in the manufacture of superphosphate (SSP) was employed.

In normal SSP production, diluted (70%) sulfuric acid reacts with phosphate rock. The reason for using diluted instead of concentrated sulfuric acid is probably that the viscosity of the solution is promoting the efficiency of the reaction.

An alternative way to introduce the equivalent amount of water for dilution is by mixing sulfuric acid (98%) with 31% w/w hydrochloric acid. In this way one obtains the required viscosity of the mixture which however is enriched in  $H^+$  due to the presence of HCl.

The chemical reactions corresponding to each case are:



Thus acidulation of the phosphate rock is obtained by the mixture of HCl/ $H_2SO_4$  which not only solves the problem of the abundance of HCl but also reduces essentially the cost of the final product (SSP) as HCl is substituting part of  $H_2SO_4$ .

Due to the presence of  $CaCl_2$  as inert which replaces part of the  $CaSO_4$ , the final product is slightly more hygroscopic than conventional SSP. However it is slightly richer in  $P_2O_5$ . It also contains a small quantity of chlorides ( $\approx 7\%$ ) which is agronomically acceptable.

The production of SSP by substituting ca 15% of the sulfuric acid with hydrochloric acid was effected in the Broadfield Den without major problems. Special precautions were taken to avoid pollution problems regarding emission of hydrochloric acid fumes.

To this end it was decided to premix sulfuric and hydrochloric acid prior to acidulation. This was also the limiting factor for not increasing the percentage of substitution of sulfuric by hydrochloric acid.

## 9. SUMMARY / CONCLUSIONS

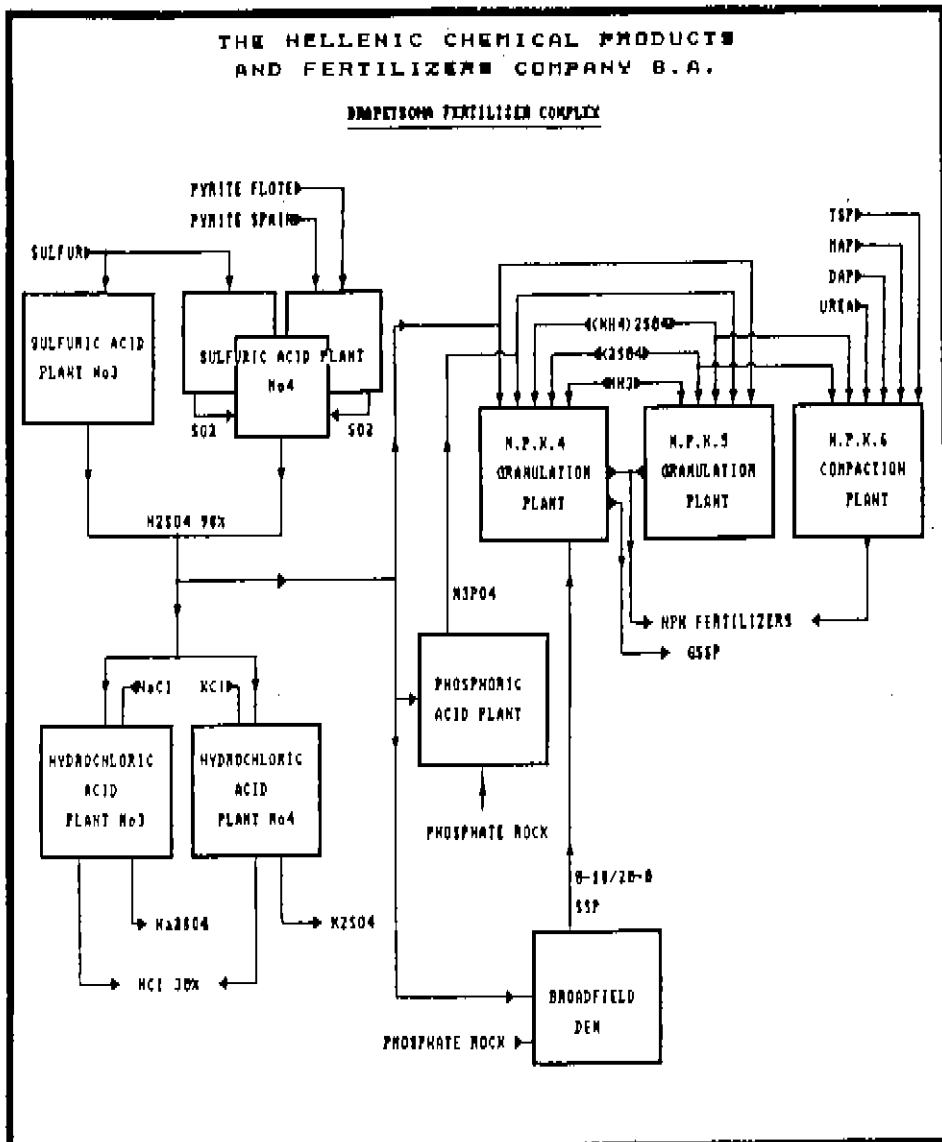
It is true that each fertilizer plant in each country has its own individual peculiarities. The message coming out of this presentation is however that in each case there are several simple steps which can assist in the reduction of the cost.

One way to do this is by recycling in the fertilizer production process useful materials coming from other sectors of the industry like for example vinasse which can replace a small part of potash or HCl which can replace part of the sulfuric acid, or phosphogypsum as inert material.

Another way is to increase the degree of utilization of existing equipment for production of alternative products like for example in the case of production of magnesium sulfate in a Broadfield Den.

Finally, it is worthwhile to note that even such a common subject like heat recovery can always find new applications like for example in evaporation of anhydrous ammonia by hot water heated by sulfuric acid.

FIG.1



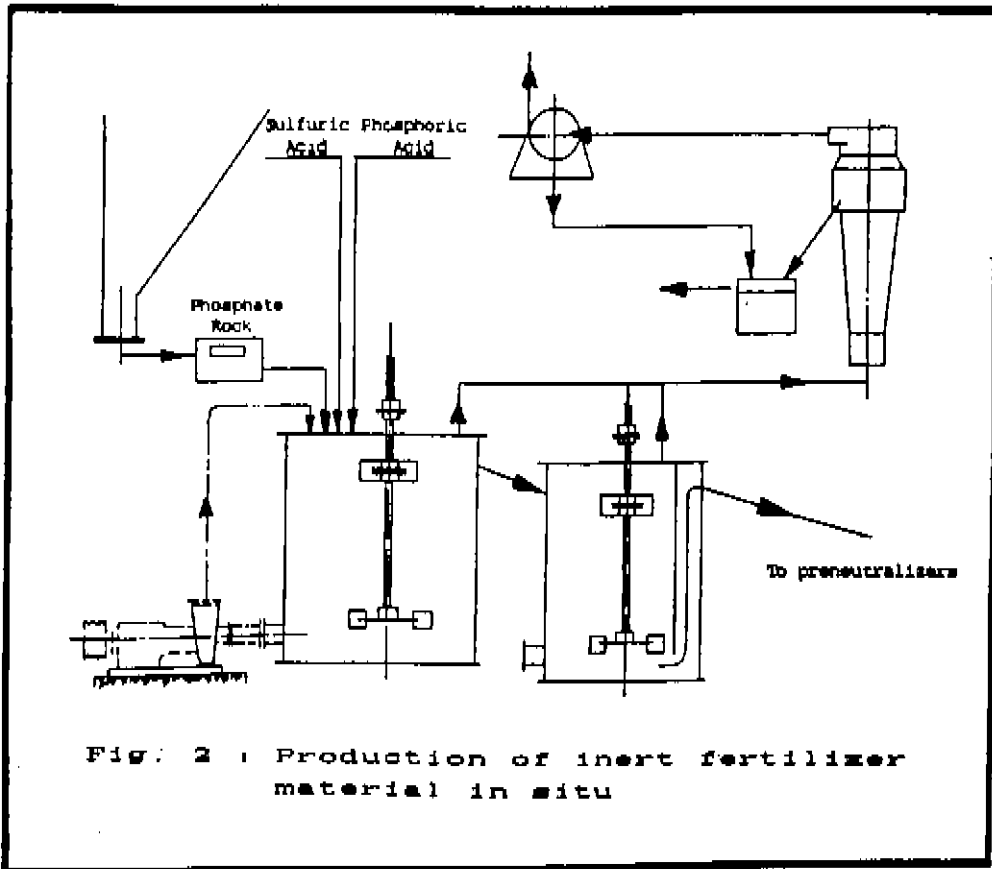


Fig. 2 : Production of inert fertilizer material in situ

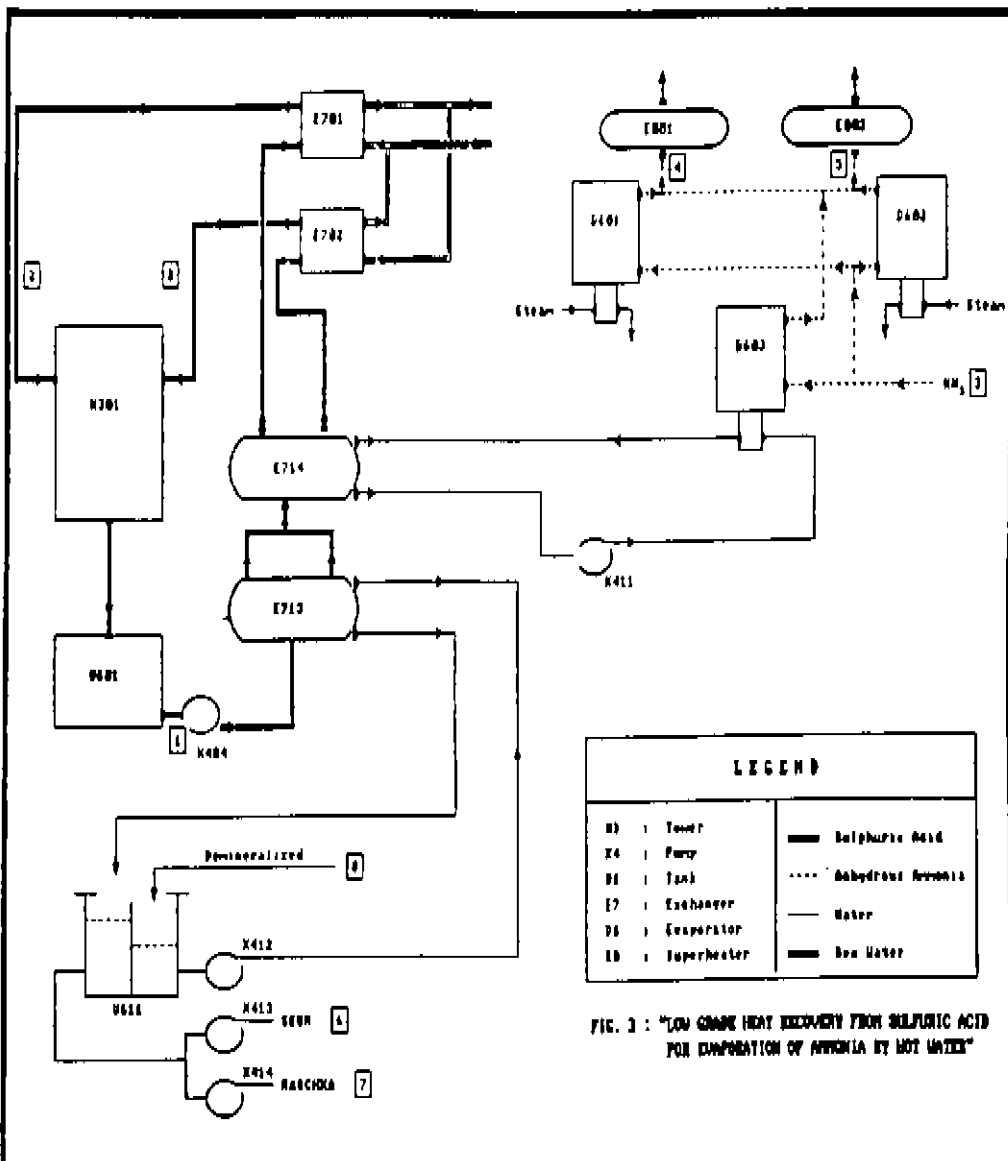


FIG. 3 : "LOW GRADE HEAT RECOVERY FROM SULFURIC ACID FOR EVAPORATION OF AMMONIA BY HOT WATER"

## 6. PRODUCTION OF INERT FERTILIZER MATERIAL IN-SITU

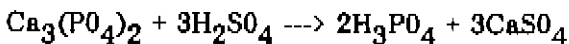
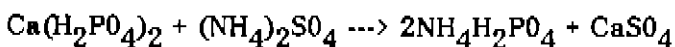
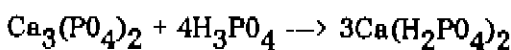
Although the general trend is to produce fertilizer grades which contain the highest possible concentration of fertilizer elements, it is still desirable to produce certain formulations such as 16-20-0, 11-15-15, 12-12-12, etc, which have to be balanced by inert material. Such inert materials commonly used are limestone, natural gypsum or sand, etc.

Phosphogypsum is also a possible alternative. However, in most cases it is a very difficult material to handle and therefore it is rarely used as such.

To overcome the above problem HCPF had long ago introduced a process for production of inert phosphogypsum in situ, i.e. just before the main neutralization step of phosphoric and sulfuric acid by anhydrous ammonia. The process involves acidulation of phosphate rock by the phosphoric acid to be used in the preneutralizer as well as by small quantities of sulfuric acid and ammonium sulfate solution (which is a by-product of a sulfuric-acid tail-gas treatment plant).

The required amount of calcium to produce the amount of inert gypsum needed in the fertilizer plant is furnished from the phosphate rock.

The reactions taking place are:



The resulting slurry is subsequently fed to the preneutralizer where it is reacting with the rest of the sulfuric acid required as well as with anhydrous ammonia.

In the case of 16-20-0, 60-80 kgs of rock are required per ton of final product. This amount of rock is attacked by the phosphoric acid before it is fed to the preneutralizer. 40-50 kgs of sulfuric acid (98%) are also added to the reactors. The slurry which is produced contains about 10-15% of solids while the filtrate corresponding to this slurry has a  $\text{P}_2\text{O}_5$  content of 33-35%.

The advantage of the above process, apart from the production of inert material at almost zero cost as it is directly fed in the main fertilizer slurry, is that it produces equivalent in a more concentrated phosphoric acid thus saving energy saving in the fertilizer drying process. Moreover the way in which the inert material is introduced in the main fertilizer slurry ensures that this inert material is uniformly distributed in the fertilizer granule thus enhancing the strength of the granules.

The gases resulting from the above reaction are scrubbed in the final scrubber of the NPK plant with sea water since the main pollutant is fluorine. It should be noted that during the above process the main portion of fluorine remains in the liquid phase. Therefore the fluorine in the gas-phase (including that in the preneutralizer off-gases) is much lower than the preneutralizer conventional NPK production.

## 7. PRODUCTION OF MAGNESIUM SULFATE IN A BROADFIELD DEN

Magnesium is the most common of the secondary elements incorporated in special fertilizers. The most common source of water soluble magnesium is magnesium sulfate which is commercially available either as kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) with 27% content in  $\text{MgO}$  or as epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) with 16% content in  $\text{MgO}$ .

Both forms are prepared by the action of sulfuric acid on magnesium carbonate or hydroxide. The chemical reaction is followed by a separation/crystallization process to obtain the final product.

HCPF is producing several special fertilizer grades with micronutrients utilizing the advantages of a compaction plant for such case. As magnesium sulfate is widely used in these grades it was decided to produce it instead of importing it. However the equipment cost for the reactors, crystallizers etc was not justified by the rate of production. Thus after extensive laboratory tests it was shown that magnesium sulfate could be produced at acceptable quality level by utilizing the spare capacity of a Broadfield Den, which was normally used for SSP production.

The two cases (production of SSP or magnesium sulfate) present several common points, as in both diluted sulfuric acid is used to acidulate a solid material (phosphate rock or magnesite  $MgO$ ). In both cases one has to search for optimum conditions as far as the efficiency of reaction and quality of the product is concerned among the most important operating parameters such as density of the sulfuric acid, granulometry and impurities of the solid raw material etc.

The final product from the Den is a relatively dry (moisture  $\approx$  7%) crystalline powder and after several days of curing, is ready for use. It is actually a mixture of kieserite and epsomite with a water-soluble  $MgO$  around 20% and a total  $MgO$  content around 27%.

## 8. AMMONIA EVAPORATION BY HEAT RECOVERED FROM SULFURIC ACID PLANTS

The advantages of using gaseous instead of liquid anhydrous ammonia either in the preneutralizer or in the granulator in a typical NPK plant are beyond any doubt. In order to save energy, steam used for the evaporation of ammonia can be replaced by hot water which in turn is heated by low grade heat recovered from the absorption tower of a sulfuric acid plant.

The low grade heat available from this part of the sulfuric acid process could of course be used alternatively in various other energy consumption centers such as phosphoric acid evaporation. However due to lack of the relatively higher capital required for such a project, it was decided to use the recovered heat as a first step for boiler feed water heating and at a second step for ammonia evaporation. The first step of the project is already in operation. The second step is at the stage of procurement of equipment.

The basic idea is to recover heat from the intermediate absorption tower of a 700 tpd sulfuric acid plant via a shell and tube special alloy acid cooler whereby demineralised water is heated by hot sulfuric acid at about 45°C.

This hot water is used to evaporate ammonia in a Kettle type ammonia boiler which is supplying the gaseous ammonia to the NPK plants.

The system will save around 34000 tpy of steam used so far for ammonia evaporation. It will to save equivalent amount of high pressure steam from the sulfuric acid plant which will be transformed to electric power. The payout period of the project is thus expected to be around two years.



## 9. SUMMARY / CONCLUSIONS

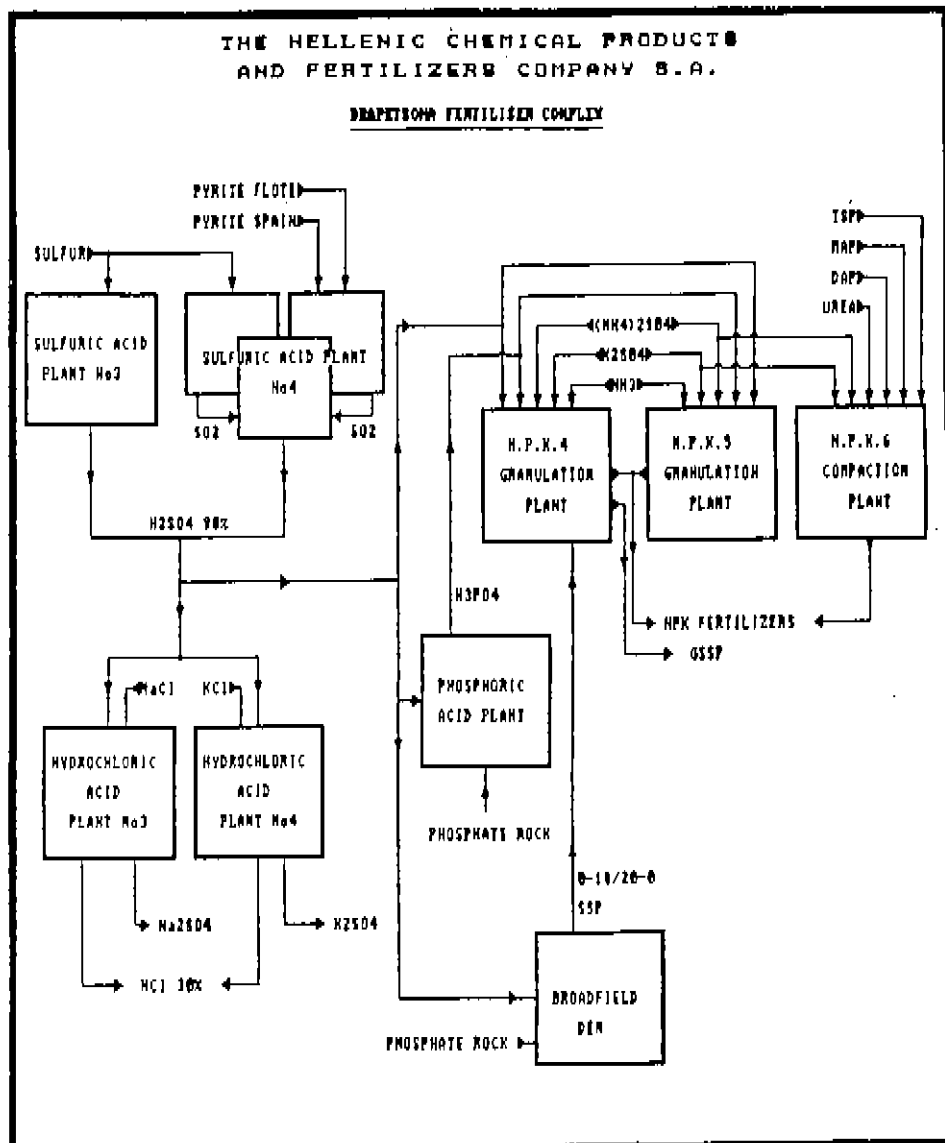
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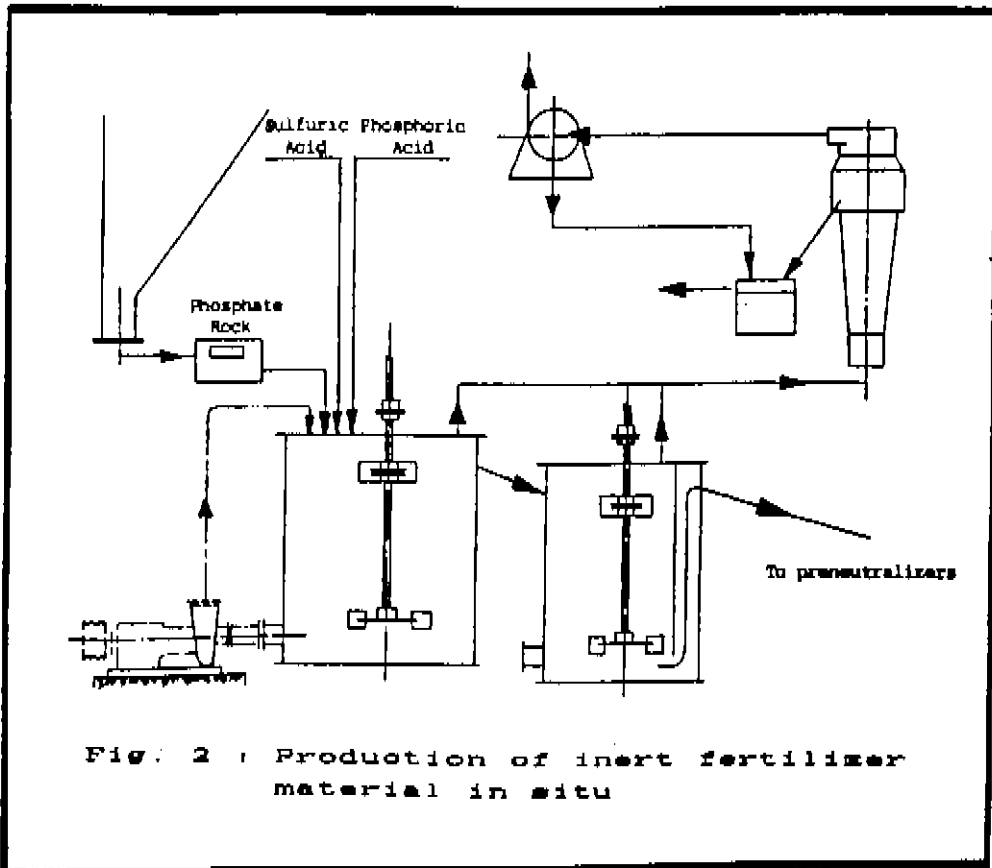


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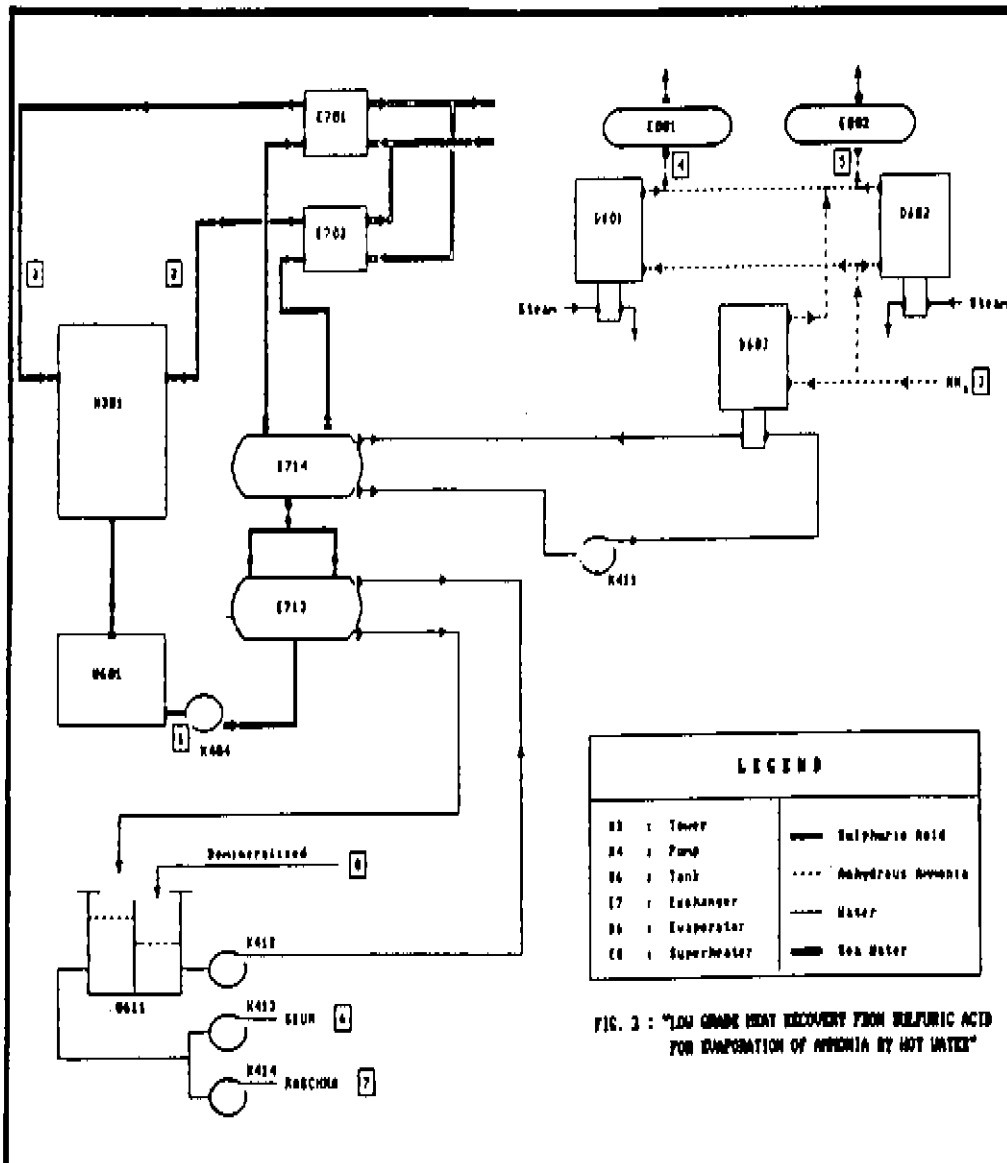


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