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UTILIZATION OF BY-PRODUCTS FROM THE WET
PHOSPHORIC ACID PRODUCTION TO PREVENT
ENVIRONMENTAL POLLUTION[1]

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INTRODUCTION

The science of futurology has made forecasts at what time mankind could perish because of environmental pollution produced by men. We find it difficult to share such pessimistic Utopia, but we are nevertheless convinced that gigantic efforts will be necessary to maintain at a tolerable level the environmental conditions for the survival of the human race.

Producers of phosphoric acid are facing difficult problems in this respect and are being constrained by governmental agencies with increasingly strict specifications to be met. In the production of wet phosphoric acid approx. 4,5 ts of gypsum as dry dihydrate is obtained as byproduct per ton of P_2O_5. Commercial phosphate contains 100 - 150 kgs fluorine/t P_2O_5 of which 40 - 50 kgs are volatilized in the course of the concentration step in form of SiF_4 and HF resp. The safe disposal of these compounds is possible only at considerable costs. Utilization as raw-material for other products can reduce these costs or even be profitable. So in the following, these possibilities which have been realized in part by our Company, will be described.

I. USES OF BYPRODUCT GYPSUM

Our Company produces approx. 600 000 tons of Complex-fertilizer per year using phosphoric acid. The disposal of gypsum however is not possible or very costly.

Therefore all possibilities of utilization of gypsum have been studied and some of them have been realized.

4,5 tons of gypsum as dry dihydrates is obtained per t P_2O_5; this produces amounts to 450 ts/day gypsum per 100 ts P_2O_5 or more than 2 million tons in a 500 000 ts per year plant. The utilization of gypsum is possible in building industry as setting controller for cement, as plaster, for plaster boards, wall blocks or in the fertilizer industry for the production of ammonium sulfate,   or alternatively for both in the production of sulfuric acid and cement clinker.

A) Purification of phosphorgypsum

So, on the one hand, more than 60 million ts of this byproduct gypsum are manufactured per year, on the other hand, however, approximately the same quantity of natural gypsum is won every year and is used for the above mentioned purposes.

Why cannot natural gypsum simply be replaced by byproduct gypsum? This is, of course, primarily a question of the costs, and the costs of byproduct gypsum accrue in most cases from the drying and purification processes. Here an important role is played by the impurities of gypsum, which may considerably influence its further uses. In byproduct gypsum they result from its origin, where as in natural gypsum they are absent. The impurities may differ greatly depending on the crude phosphate rock from which they are derived, but also the process of attack (dihydrate, hemihydrate, hemihydrate-dihydrate, dihydrate-hemihydrate) and its variations effect the properties of the gypsum. The information given in technical literature about gypsum, produced from the same phosphate rock and after the same process, shows great differences. The most important impurities in gypsum are organic products (up to 0,2 % C), soluble and insoluble P_2O_5 (up to 2 %) and soluble and insoluble fluorine (sometimes over 2 %). A certain degree of purification is reached by washing (soluble P_2O_5 and F) and flotation (above all C). A still better effect can be achieved by calcinating, and if needed, adding certain additives, suspending, filtering and calcinating. The greatest purification, however, is secured by converting the gypsum from one crystal form into another; this may occur either during the course of the P_2O_5 production in the hemihydrate-dihydrate processes or dihydrate-hemihydrate processes, or it may occur separately, like in a German process, in which dihydrate is suspended and then recrystallized under pressure to form hemihydrate. Thus qualities of gypsum may be manufactured which contain less than 0,02 % C, 0,1 % P_2O_5 and 0,1 % F and are of universal applicability.

This purification process will of course be carried out only as far as the resulting products require. The demands on the purity of the gypsum may differ, depending on the quality of the requested plaster and plaster boards, or when the gypsum is to be used for cement, ammonium sulfate, ammonium nitrate carbonate or the gypsum-sulfuric acid process. In each case the purification process will depend on 1. the phosphate rock, 2. the process of attack, 3. the ensuing impurities in the gypsum and 4. the ultimate applications the gypsum has been designed for.

B) Gypsum in construction industry

In the grinding of cement clinker gypsum is usually added in quantities of 3 - 4 % to act as setting controller; recently byproduct gypsum has increasingly come into use.

Japan is not rich in natural gypsum and the existing deposits are of poor quality. Consequently Japan was the first country to employ byproduct gypsum for construction purposes in 1934. Today approximately 3 million ts byproduct gypsum are estimated to be used in Japan in the construction industry per year, half of it as setting controller for cement. Because of this application of gypsum Japan has first developed phosphoric acid processes, like the hemihydrate-dihydrate process, in which gypsum containing less than 0,3 % P_2O_5 and less than 0,2 % F can be obtained. In Europe, too, this phosphorgypsum, mostly from the dihydrate-hemihydrate process, is widely used as setting controller.

The use of byproduct gypsum for plaster, plaster wallboards and building blocks has, starting from Japan, gained importance throughout the world. Above all in the case of plaster-boards and building blocks a treatment by recrystalization of the di-hydrate to α -hemihydrate has proved especially efficacious. By maintaining certain reaction conditions and adding various additives the properties of the manufactured product may be exactly preplanned.

More and more chemical plants have turned to utilizing their by-product gypsum for construction industry. Only recently the technical papers reported of a house made of byproduct gypsum in which even the exterior walls of the pre-fabricated construction elements were of gypsum.

The more expensive the disposal of byproduct gypsum will become due to the legal regulations imposed to protect the environment, the more economical it will get to use byproduct gypsum in construction industry even where there exists enough natural gypsum.

C) Gypsum in fertilizer industry

The first utilization of byproduct gypsum in our company was the production of ammonium sulfate (table 1). The well known Merseburg process can be applied also to byproduct gypsum after suitable pretreatment. Our plant was started up in 1952 and produced 600 ts/day ammonium sulfate from byproduct gypsum. We have licensed the process to the Stickstoffwerke Krefeld in Germany, to the FACT Comp. in India and to Reserve Oil and Gas Company in California. The German plant started 1958 with 150 ts/day ammonium sulfate. The Indian plant has produced 300 ts/day ammonium sulfate from byproduct gypsum since 1966, the Californian plant has produced 100 ts/day since 1969 from natural gypsum but is planned to be converted to byproduct gypsum.

The byproduct of carbonate of lime obtained may be utilized for calcium ammonium nitrate, as fertilizer lime or as raw material for the cement industry. Unfortunately the use of ammonium sulfate is only possible for certain agricultural purposes and not under every climatic conditions. The price of ammonium sulfate and the sales opportunities were greatly reduced in recent years due to large amounts of ammonium sulfate obtained as byproduct in the caprolactam and acrylonitrile production.

The processes for acrylonitrile and caprolactam production have, however, been so greatly improved recently that no or only little ammonium sulfate is obtained. Thus, ammonium sulfate has become a product very much sought after and its manufacture has become interesting again.

D) Gypsum for sulfuric acid and cement

The last example of gypsum utilization is the production of sulfuric acid and cement clinker (Table 2). In the well known Müller-Kühne process SO_2 and cement clinker is produced in a rotary kiln, using natural anhydrite, clay, sand and coke as raw materials; SO_2 is converted to sulfuric acid in the usual manner. A high quality cement clinker for Portland cement is obtained if the raw material composition is appropriate. Due to the development on the sulfur market and because of the high investment costs of a gypsum sulfuric acid plant this process is not attractive at the time being, with anhydrite or natural gypsum as raw materials. We have modified the process and are able to use byproduct gypsum instead of anhydrite. The CISA Company, South Africa, has put a 350 ts/day sulfuric acid plant on a byproduct gypsum basis on stream in August 1972 using our licence; this plant is scheduled to be expanded to 1 000 ts/day.

On the basis of laboratory experiments we have replaced increasing quantities of anhydrite by byproduct gypsum in the raw material and are now able to replace it completely. So we reach a circulation of the sulfuric acid used in the phosphoric acid production, while calcium from the phosphate is used for the production of Portland cement.

Apart from the drying of gypsum two points have to be emphasized: P_2O_5 and fluorine-content of this gypsum may affect the setting behaviour of the resulting cement. Fluorine compounds may act as

flux and may therefore lead to crusts in the kiln; they are also detrimental in the gas since they act as catalyst poisons in the sulfuric acid production. According to our findings we can point out that the cement clinker meets the highest quality demands and no detrimental effects are observed in the sulfuric acid production if contaminations in gypsum (based on dihydrate) do not exceed 0,5 % P_2O_5 and 0,15 % fluorine. These concentration limits can be realized without difficulties by purification the gypsum or in some P_2O_5 processes directly.

As a second essential improvement a heat exchange unit for pre-heating of the raw material was installed. In a preheating unit common in cement industry the raw material will be heated up by SO_2-containing gases from the rotary kiln. Due to this installation a considerable reduction of the specific heat requirements can be reached. By adding this preheater to an existing rotary kiln the production capacity can be increased by about 20 %. The investment for a new plant with preheater is lower then that for a plant of the same capacity without a preheater.

B) Conclusion

In order to conclude the gypsum problem we would like to empha-sise that there is no universally applicable solution to gypsum utilization. Each case must be considered on its individual merits in order to achieve maximum economic success. Essential for the chosen solution is the geographical location of the plant, this is important not only because of raw material cost but also be-cause of legal and marketing conditions, especially in utilising gypsum in the construction trade.

II. USES OF BYPRODUCT FLUORINE

The second pollution problem in phosphoric acid production is the fluorine content of raw phosphates; phosphates contain between 3 - 4.5 % fluorine in the form of fluorine apatite. Depending on the process the fluorine is distributed in the phosphoric acid, the byproduct gypsum, the off gas and the waste water. The fluorine content in the phosphoric acid and in gypsum is not important in many cases. It can be reduced by various methodes. Fluorine in off gas however can lead to great damages in plant growth. Therefore, gowernmental agencies issue severe legal restrictions. Condensation with water leads to formation of fluosilicic acid which can only be removed after neutralization, in some cases not even then. Also in this content legal restriction became increasingly severe.

A) Quantities of Fluorine in question

The world reserves of phosphate are approx. 60 billion ts, corresponding to 2,4 billion ts fluorine. The world production of raw phosphate is approx. 100 million tons/year; this corresponds to 4 million ts of fluorine. This is about twice the present demands on fluorine. The world consumption of fluorspar its approx. 4 million ts corresponding to approx. 2 million ts fluorine per year. The known world reserves are about 75 million tons calcium fluoride, corresponding to 37 million ts fluorine. This reserves cover the demand for only 20 years. The fluorine reserves in phosphate are thus higher by a large factor than the presently almost exclusively used raw material. However not the entire fluorine in raw phosphate can be recovered.

We shall consider fluorine in wet phosphoric acid production only. The following assumptions can be made as guidelines if considerable scattering in the composition of different phosphates and in different processes occurs. In the attack approx. 10 % of the fluorine escape in the off gas, approx. 25 % of fluorine remain in precipitated gypsum, 40 % in the vapours of concentration and 25 % in the concentrated acid.

Fluorine content in gypsum and in phosphoric acid can be considerably reduced by special procedures such as hemihydrate process or addition of silica in the attack. Due to these methodes the utilizable quantities of fluorine can be considerably increased. Utilization of fluorine is most appropriate in concentrating of the acid; there approx. 40 - 50 ts of fluorine per 1,000 ts P_2O_5 are evolved, which have to be removed or utilized. A world production fo 13 million tons P_2O_5 per year puts therefore 600 000 ts fluorine at disposal.

Fluorine is obtained as HF and SiF_4 in air and steam. Scrubbing with water produces a 15 - 25 % solution of fluosilicic acid. This acid is still frequently removed with waste water. This kind of removal is increasingly restricted due to legal measures. It is frequently necessary to neutralize with lime and subsequently remove the suspension of calcium fluoride and silica in rivers or any other safe disposal which may be costly. Estimates of these costs amount to 5 - 10 US $/t P_2O_5. Therefore, there are two convincing reasons to utilize fluorine from phosphates:

1. Lack of fluorspar and accordingly high cost
2. Profitable utilization of a byproduct which otherwise causes expensive safe removal or deposition.

B) Possibilities of use

The question is which area of fluorine chemistry offers possibilities for this undesirable waste acid. Approx. data concerning the utilisation of fluorspar are shown in figure I.

Consumption of calciumfluoride is approx. 4 million tons/year. Of this quantity approx. 40 % is used in steelworks, 5 % in ceramics and glass industry und 55 % in HF-production of which the aluminium industry uses approx. 40 %. 45 % of HF are used in the production of fluorcarbons and 15 % for fluorine, uranium hexafluoride, inorganic salts etc.

In principle all fluorine compounds became accessible if calcium
fluoride or HF resp. is prepared from fluosilicic acid. It is
also possible to produce aluminium fluoride or cryolite directly.
In any case silica must be removed which can be done in different
ways even though it is not always a simple proposition.

C) Reactions from Fluosilicic Acid (Figure II)

SiO_2 can be separated after reaction with ammonia and fluorspar
can be obtained by addition of lime to the ammonium fluoride
solution. Ammonia can be recovered except for small losses. HF
can be prepared from the ammonium fluoride solution directly by
addition of sulfuric acid, which causes also formation of ammo-
nium sulfate which is not always desirable.

Another way to obtain HF from ammonium fluoride utilizes the ter-
mic decomposition of sodium hydrogen fluoride into sodium fluo-
ride and HF; a recycling of ammonia and sodium fluoride is
necessary. An elegant method to obtain HF from fluosilicic acid
uses the decomposition by distillation into HF and SiF_4; HF is
dissolved in an organic solvent and purified by distillation
therefrom. SiF_4 is hydrolyzed to yield SiO_2 and H_2SiF_6 which is
recycled after separation of silica Investment costs and ener-
gy requirements for this process are, however, estimated to be
rather high.

Then are essentially two processes to produce AlF_3 without any
HF-formation. One way goes via ammonium fluoride to produce
ammonium cryolite as an intermediate which is thermally decom-
posed with additional aluminium hydroxide into aluminium fluo-
ride and ammonia. The other way in which fluosilicic acid
reacts directly with aluminium hydroxide, shall be discussed
in detail later on. Cryolite can be obtained from fluosilicic
acid via sodium fluoride with AlF_3 or aluminium hydroxide and
CO_2. Sodium fluoride is accessible via ammonium fluoride or

directly from the acid with sodium carbonate. In both cases re-cycling is necessary, in one case ammonia, in the other one CO_2 and soda. The second way requires high dilution because of the low solubility of sodium fluoride.

D) Direct AlF_3-Process (Table 3)

The aqueous fluosilicic acid is reacted directly with aluminium hydroxide whereby silica precipitates and AlF_3 is formed as a metastable solution. Under appropriate reaction conditions sili-ca is obtained in an easily to sediment form; factors in this process are the purity of the components, the mixing ratio, the temperature, stirring, etc. Silica is quickly removed by centri-fuging and subsequently washed. The supersaturated AlF_3-solution is mixed with seed crystals in order to initiate crystallization. Crystallization requires approx. 5 hours and therefore several individual crystallizers are suggested to be used. After approx. 5 hours AlF_3 has crystallized as trihydrate (except for a resi-dual concentration of 20 g/l) and can be separated by centri-fuging. The washed trihydrate is dried and calcinated. Calci-nating is an essential step in this process since water hydrolyzes AlF_3 at high temperature forming HF and aluminium oxide, but can-not be removed completely below this critical temperature range. The hydrolysis reaction proceeds very slowly below 200 $^{\circ}$C but 85 % of the water can be removed under formation of aluminium-fluoride hemihydrate. Calcination is therfore carried out at approx. 200 $^{\circ}$C in a disk drier or a fluid bed and completed at 560 - 600 $^{\circ}$C by means of an indirect heated fluidized bed in an air stream. This calcination process is a special design and has proven to be very successful. The endproduct is cooled and can be packed.

A few comments have to be added on the quality of the raw materials, the endproduct and on the energy consumption. There is no difficulty to obtain fluosilicic acid with 17 - 25 % con-centration in the scrubbers of a phosphoric acid concentration

unit; however special precautions have to be taken to keep the P_2O_5-content low. Off gas containing HF and SiF_4 must be freed from P_2O_5-droplets by means of a prewashing procedure or by means of a demister. The tolerable limit of 250 mg P_2O_5/l can be reached without difficulties; competent companies guarantee as low as 50 - 70 mg. Chlorine determines the choice of material. Above 1 g/l (only in acid from Israel phosphate) corrosion of stainless steel occurs and therefore a rubber lining of all the equipment is necessary. Aluminium hydroxide is commercial grade.

The endproduct contains 96 % guaranteed AlF_3-content (even 98 % can be reached) and thus has the best purity of all commercial products. Particle size analysis indicated 5 % above 0.2 mm and 6 % below 0.05 mm. The raw material and energy consumption can be seen on table 3. The yield of approx. 80 % (relative to fluorine and aluminium) is not very satisfactory; yet the process produces considerable economic advantages. Losses are mainly due to solubility in mother liquor and can be greatly reduced when recycling into off gas scrubbing of the phosphoric acid concentration or in other ways such as simultaneous production of cryolite. So a yield of more then 90 % can be reached.

The production cost with fluosilicic acid as a raw material are below the costs for raw material and energies starting with fluorspar at 95,- US $ per ton. The investment is lower then that for a plant with the same capacity starting from fluorspar via HF. The question why AlF_3 is still made from fluorspar is somwhat puzzling and there is no logical answer to it. Future may however lead to new plants based on fluosilicic acid and existing plants based on fluorspar may gradually be closed down. The HF-sections of such plants may be utilized to satisfy the growing demand of HF for fluorcarbons.

Our plant for 2 000 ts/year is now operating since ten years. We have licensed the process twelve times in Rumania, East Germany and Japan, Sweden and Jugoslavia.

The plant with the highest capacity up till now will start this year in Sweden producing 15 000 to a year of AlF_3.

5) Conclusion

The brief review about possible solutions of the fluorine problem in the phosphoric acid production showes a lot of interesting reactions. All of them were studied all around the world. While for the reaction of the gypsum problem a lot of different processes are in operation is for the waste fluorine only the aluminium-fluorid process used in a technical scale. This process is an economic solution for a pollution problem under almost any circumstances. The only problem in this context is the sales situation; this leads in some instances to cooperations between P_2O_5 and aluminium producers like the new plant in Sweden.
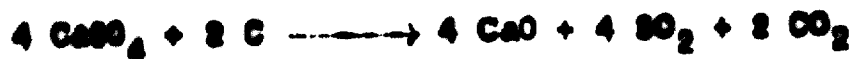
Table 1. Ammonium Sulfate

$$2 \, NH_3 + CO_2 + CaSO_4 + H_2O \longrightarrow (NH_4)_2SO_4 + CaCO_3$$
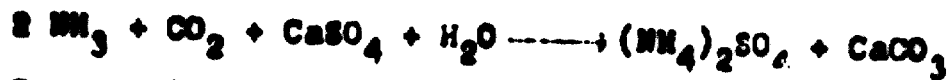
Consumption figures per metric ton $(NH_4)_2SO_4$:

$CaSO_4 \cdot 2 \, H_2O$	1,31	ts	Cooling water	50	m3
NH_3	0,27	ts	Steam	0,65	ts
CO_2	0,35	ts	Electric power	61	kWh
H_2SO_4	0,098	ts	Air	10	Nm3
Process water	1,5	m3	Fuel	0,43	Mio kcal

Rough investment figure: 5 Mio US $ for 100 000 ts/y

Table 2. Sulfuric Acid and Cement

$$4 \ CaSO_4 + 2 \ C \longrightarrow 4 \ CaO + 4 \ SO_2 + 2 \ CO_2$$

Consumption figures per metric ton sulfuric acid and about one metric ton of cement clinker:

Gypsum	2,5 ts	Fuel	3 Mio kcal
Clay	140 kgs	Electric power	230 kWh
Sand	80 kgs	Cooling water	65 m3
Coke	95 kgs		

Rough investment figures: 22 Mio US $ for 1 000 ts/day

Tabld 3. Aluminium fluoride from
Fluosilicic acid

$H_2SiF_6 + 2 Al(OH)_3 \longrightarrow 2 AlF_3 + SiO_2 + 4 H_2O$

Consumption figures per metric ton AlF_3:

$Al(OH)_3$	1,17 ts	Fuel		1,12 Mio kcal
H_2SiF_6	1,1 ts	Electric power	212	kWh
		Steam	1,5	ts
		Air	400	Nm3
		Cooling water	140	m3

Rough investment figure: 3 Mio US $ for 5 000 ts/y
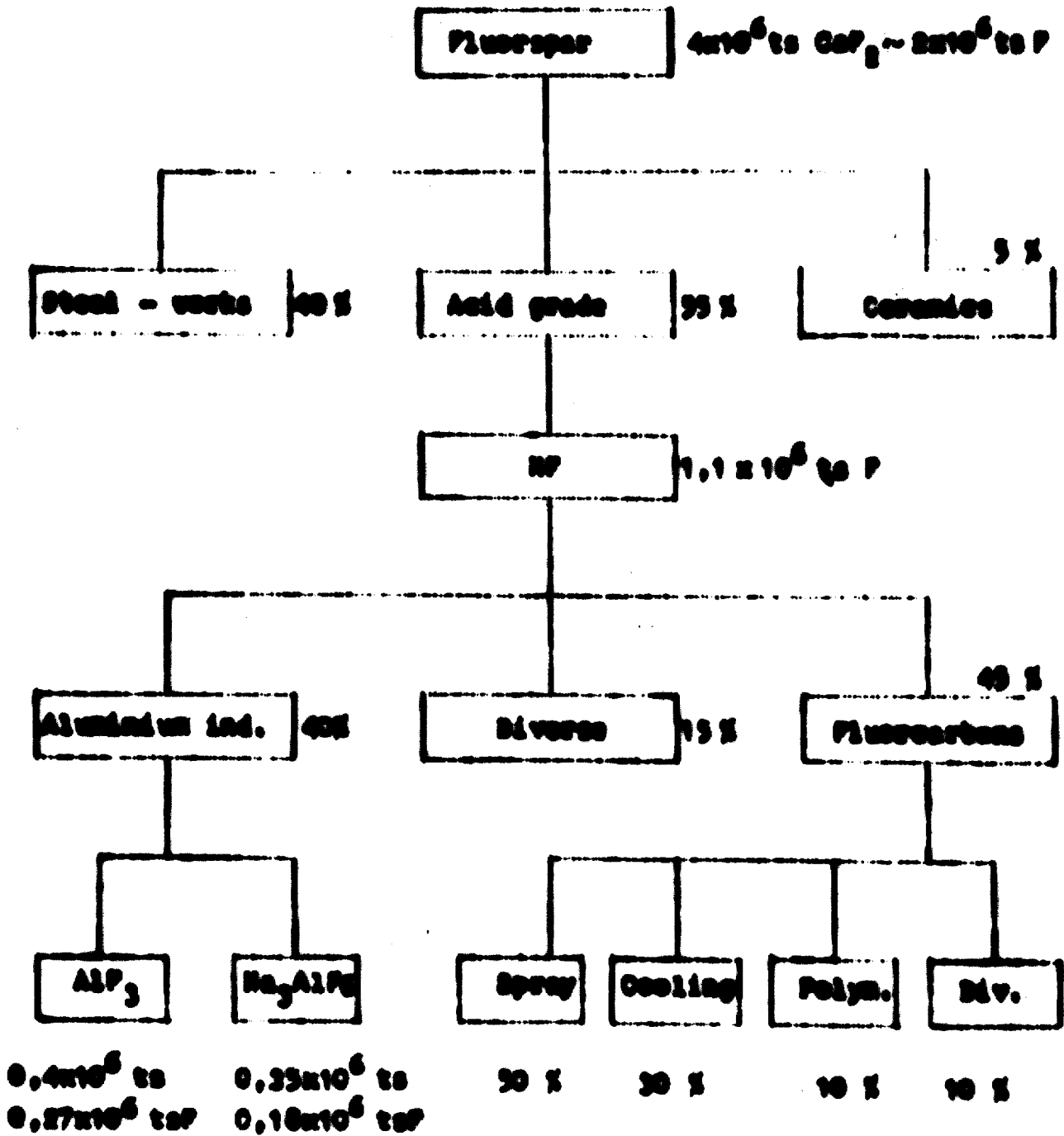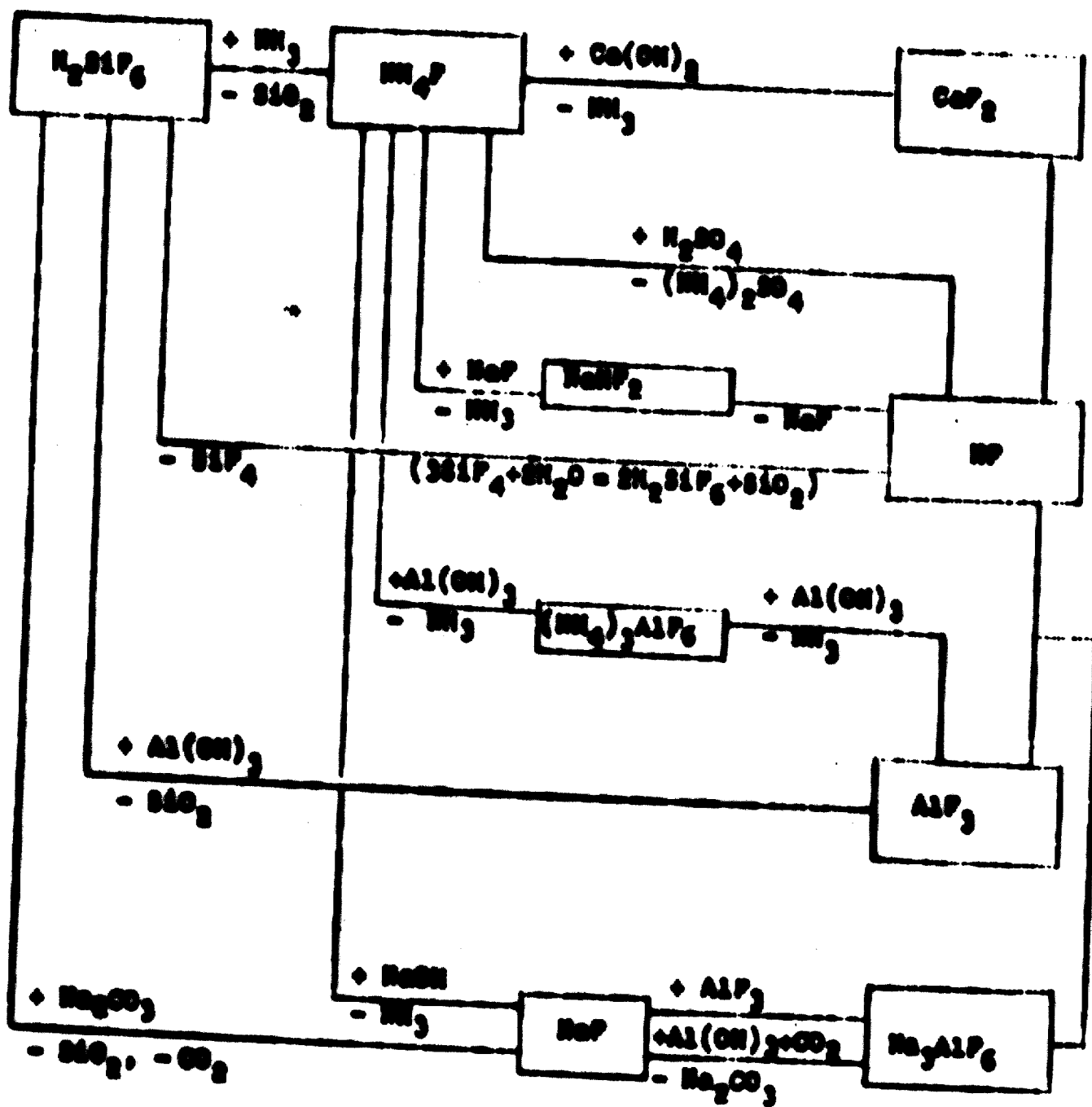4,5 Mio US $ for 10 000 ts/y

Figure 7. Fluorspar consumption/year

Figure II. Products from
Fluosilicic acid

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