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REVAMPING AND ENERGY COST REDUCTION OBTAINED IN ONE OF MONTEDISON'S
PHOSPHORIC ACID PLANTS WITH LOW INVESTMENT COST.

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INTRODUCTION

The phosphoric acid manufacturing plant discussed in this paper went
on stream in 1961 within a fertilizer factory where fertilizer manu
facture involved the following steps:

- Sulfuric acid manufacture to obtain superphosphate and phosphoric
  acid;

- Use of superphosphate as the basic raw material to the NPK fer
  tilizer manufacturing operation, that is, fertilizers of a low-
  -grade type containing only ammonium nitrogen. This operation
  was carried out in an old plant that had originally been used to
  granulate superphosphate only (approx. 120,000 tons/year);

- Phosphoric acid conversion into diammonium phosphate 18.46.0 in the
  form of granules for sale. The manufactoring unit capacity was
  about 30,000 tons P_2O_5 per year.

Subsequent technological developments led to a process featuring an
acid treatment of phosphate rock with both sulfuric and nitric acids
as a means of producing mixed fertilizers. The above process was
implemented in two twin units having each an individual capacity of
approx. 200,000 tons per year and in a new nitric acid plant.

Increasing market demand for fertilizers carrying higher and
higher grade of produced NPK P_2O_5 led the company to use larger and
larger quantities of phosphoric acid instead of sulfuric acid as the
binding agent for phosphate rock calcium. (In fact, our attack of the
phosphate with nitric and sulfuric acid does not separate calcium)

Additional economic and marketing considerations pointed out the op
portunity for our company to further expand the output of each of
its nitric attack units to about 300,000 tons/year for each.

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At the same time, the decision was made to stop our diammonium phospha te operation, and to use most of the available phosphoric acid in the acid treatment of phosphate rock together with nitric acid.

The above decision led to a shortage of H_3PO_4 and to the need for our company to buy P_2O_5 (in the form of H_3PO_4 or diammonium phosphate) from independent producers.

The steady manufacturing level in our phosphoric acid unit, and the general shortage of P_2O_5 prompted us to study the existing facilities and work out a strategy to

a. expand the plant capacity to produce up to 50,000 tons P_2O_5 per year, and lower the operating costs at the plant battery limits;

b. integrate the plant as much as possible with the rest of our fac tory as a means of reducing operating costs outside the plant as well.

ADOPTED CRITERIA

The decision to revamp a preexisting plant or to erect a new one must not be made only on the basis of the company's industrial policies and strategies and financial resources as available to it.

An element that cannot be overlooked is the return on investment, and consequently the decision to revamp an existing plant may be sound provided that the cost of the project is low and a satisfactory pro fitability level may be expected from it.

However, profitability per se is not the only criterium by which the decision to revamp should be evaluated. Any revamping project must also provide a certain degree of competitive capacity, which means putting the revamped plant in the position to compete with facilities that adopt new technologies and, in particular, with plants which were designed in such a way as to keep their operating costs and their energy consumption as low as possible, not to mention their undoubted ly more advantageous scale.

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That's why any revamping project must secure a "quality" result, so that the revamped plant can successfully meet competition by plants adopting the most advanced manufacturing processes. And this should hold true not only on a short-term basis, but also on a medium-term one.

The foregoing considerations were at the basis of our decision to thoroughly review the operation and design of Fertimont's phosphoric acid plant.

A pilot plant was set up at the company's Research and Development Center at Porto Marghera to study and develop a few changes in the phosphoric acid manufacturing process that were subsequently transferred to an industrial scale.

No new invention was involved. Our result was obtained by applying both old and recent theories on gypsum crystallization. In the course of our development work, control procedures were refined in order to better control each parameter involved in gypsum crystallization.

Our second objective, i.e., integrate the revamped unit with the rest of the factory, was attained through the following steps:

a. Use of dilute H2SO4 resulting as a by-product from HNO3 concentration. As a consequence of this intended use of the above by-product, HNO3 concentration was carried through extractive distillation in the presence of sulfuric acid. (This procedure has been implemented for many years.)

b. Recovery of low-pressure steam as a by product of HNO3 neutralization to obtain the ammonium nitrate solution used in the two complex fertilizer manufacturing lines. (Work on this part of our project is still under way.)

GYPSUM CRYSTALLIZATION

When phosphoric acid is produced by wet process, the most critical step consists in the separation of calcium sulfate dihydrate from this acid.

This step is usually carried out in continuous filter systems, and it is heavily dependent upon the morphology and size of gypsum crystals as obtained by treating phosphate rock with sulfuric acid.

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Both the types of crystals being obtained and process conditions governing crystal properties have a direct influence on the process yield and plant capacity.

When crystals are small, heterogeneous, and bad shaped they take up too much phosphoric acid, and this acid will be hardly removed in a thorough way during slurry filtration and crystal washing. Of course, when the rate of filtration is low, the manufacturing rate of the entire process and plant capacity will be negatively affected.

Phosphoric acid plant must then be run in such a way as to generate uniform gypsum crystals with the best morphological characteristics.

Therefore, it is essential to provide the best conditions that can promote crystal growth as well as new crystal formation.

Gypsum crystallization is defined by two well-known relationships that govern crystal nucleation and their growth rate. (1)

1. $R_n = K_n \Delta C^m$

    where R_n = nucleation rate

               K_n = constant

            ΔC = supersaturation

               m = order of the nucleation rate, which was close to 2 in our case (2)

2. $R_G = K_G L^m \Delta C^n$

    where R_G = growth rate

               K_G = constant

               L = crystal size

               n = order of the growth rate, which was close to 1 in our case

               m = coefficient, which was close to 0 in our case

In order to form nuclei (1) (3), the ions here considered must go beyond a given energy barrier, that is, they must be provided with a sufficient amount of activation energy. The higher the energy barrier, the lower is the number of nuclei that possess enough energy to overcome it.

When different reactions can occur at different levels of activation energy, the reaction calling for low energy levels will occur first. That's why in the H_3PO_4 manufacturing process $CaSO_4 \cdot 2H_2O$ can be obtained under operating conditions under which the stable form is $CaSO_4 \cdot \frac{1}{2}H_2O$.

At lower degrees of supersaturation, larger gypsum crystals can be produced. The increase in the size of gypsum crystals is mainly dependent on the fact that the nucleation rate decreases more rapidly than the growth rate as supersaturation decreases. In fact, as said above, the order of the growth rate is close to 1, while that of the nucleation rate is close to 2.

As to gypsum crystallization (2), it was found that the crystal growth rate is higher at a high temperature, but the nucleation rate is comparatively low.

The critical element in the process is crystal morphology because it depends on the relative rates of growth of the individual crystal planes, to which a relationship similar to 2. applies.

Crystal morphology is substantially influenced by the presence of impurities. Their inclusion into the crystal planes may badly affect their growth rate. For example, fluorine ions (F^-) reduce the growth rate of every growth crystal planes.

Control over the crystal growth rate will be discussed below, and the distinction will be made between independent (or uncontrollable) variables and variables that can be acted upon.

Independent variables are:

- the chemical composition of phosphate rock;

- the crystalline structure of apatite, crystal size, and conditions affecting the reaction for breaking the apatite structure;

- the retention time of the slurry in the reactors.

Controllable variables include:

- the fluorine/silica ratio (it can be made optimal by adding bentonite or kieselguhr until the stoichimetric proportion for H_2SiF_6 is obtained);

- the content of P_2O_5 equivalent in the phosphoric acid produced (the influence of this variable is negligible as long as P_2O_5 equivalent is between 28 and 30%);

- the use of surface-active agents to modify the growth rate of gypsum crystals planes;

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- the solid-to-liquid ratio in the slurry (which is controlled by re
cycling the washing acid to provide optimum values for each type of
phosphate on the basis of phosphate rock reactivity);

- the reaction temperature;

- phosphate rock particle size;

- free sulfuric acidity in the slurry.

By varying the final four variables in the above list, it is possible
to control supersaturation.

As supersaturation is the prime motor of the entire process, every
condition that might lead to circumscribed and uncontrolled super
saturation at any moment must be avoided.

To do so, sulfuric acid must be dispersed at a very fast rate and in
a uniform manner throughout the slurry by very efficient stirring.

In the manufacture of phosphoric acid by wet process several operating
conditions, particularly the amount of free sulfate in the solution,
must be kept under close control.

That's why, automated analytical methods (see Appendix 1), covering
the entire analytical process (i.e., from sampling to analysis), were
developed by us.

The analytical methods we developed make it possible for us to keep
the gypsum crystallization kinetics under close control at any step
in the reaction.

In our revamped plant at Porto Marghera, the P2O5 content in slurries
is also determined automatically (see Appendix 1).

Nucleation and growth rates are also measured as reported in Appendix
2.

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THE PLANT BEFORE AND AFTER ITS REVAMPING

A block-diagram of the plant as it was before its revamping is shown in Figure 1.

It was a traditional-design plant consisting of two premixers and five reactors connected in cascade. The overall true volume of the plant was about 200 m3.

The plant was equipped with two 12-m2 Giorgini pan filters.

The characteristics of the major equipment items, the construction materials, and the installed electric power are listed in Table 1.

The plant cooling system was provided with an air-scrubber that was not continuosly operating.

Ground phosphate rock was fed to premixer 1 along with recycled, medium-strength phosphoric acid from the second section of the filter system, and with a portion of recycled slurry from reactor 4 (about 40 m3/hr).

Sulfuric acid was added in premixer 2 and reactor 1 along with the re maining portion (i.e., 50%) of the entire amount of slurry being re cycled.

The slurry in premixer 2 was fed to the reactors which operated in a cascade mode.

Reactor 5 acted as a reservoir for the filter system, and it works usually almost empty.

It was clear then that the basic requirements for effective supersatu ration control could not be met in the existing plant at our Porto Mar ghera factory.

In fact, over 98% of the acid treatment took place in reactor 1, and the downstream reactors were not adequately utilized.

The change introduced by us into the plant consisted in an axial-flow pump with a low head and a high flowrate (approx. 2,000 m3/hr) instal led downstream reactor 3 to recycle the slurry back to reactor 1.

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As shown in Figure 2, the present manufacturing cycle is completely different because sulfuric acid is fed directly to the slurry-recycling pump inlet (see Figure 3).

By the above change, more favorable conditions were created for gypsum crystallization. In particular, the present way of operating requires a lower degree of supersaturation, and the process can be controlled more easily.

Table 1 shows also the main characteristics of the equipment used for slurry recycling.

The Metal Corrosion Section of our Research Center gave an important contribution in selecting the best construction materials, mainly for impellers.

"OLD" vs "REVAMPED" PLANT OPERATION - A COMPARISON

Table 2 shows the operating conditions existing in the plant before and after the introduction of the axial-flow pump in the case of Florida 70 BPL phosphate rock.

The comparison is made on the basis of full-capacity operating conditions, that is,

   120 tons of P_2O_5 output per day by the traditional plant ("old plant")

   150 tons of P_2O_5 output per day after pump installation ("revamped plant")

The most remarkable differences between the "old" and the "revamped" plant are:

a. The new pump makes it possible to use raw rock phosphate as feeding material (i.e., rock grinding is no more necessary);

b. the reaction temperature for acidulation in the revamped plant is 4-5°C higher, and this permits using raw rock phosphate to obtain a little reduction of the amount of free sulfuric acidity into the slurry, without affecting the P_2O_5 content in gypsum crystals;

c. by the revamped plant it is possible to increase the P_2O_5 concentration in the phosphoric acid being produced, not only without reducing the filtration rate of gypsum, but rather increasing it of 25-30%.

The resulting gypsum quality could be better evaluated by microscopy, as shown by the pictures in Figures 4 and 5.

The crystals in the two pictures were obtained under completely different chemical and physical conditions.

By using unground phosphate rock, reaction kinetic problems are eliminated because crystal growth rate is increased, whereas their nucleation is reduced, and, even more important, the crystal structure is modified as a result of the low supersaturation potential in reactors 1, 2, and 3.

Unlike the situation existing in the "old" plant, in the "revamped" plant the acid treatment occurs mostly in reactor 2 up to the monocalcium phosphate.

The reaction continues in reactors 1, 2, and 3 as if the three of them were one single reactor because of the large volume of the recycling mass. Gypsum precipitation is carried out in the presence of a small amount of sulfuric acid, that is, in a condition that reduces crystal nucleation.

A new, original operating procedure was developed to use raw or coarsely ground phosphate rock. The new procedure is based on high temperature and low free sulfuric content. By the control that can be maintained over supersaturation, it is possible to obtain gypsum crystals under the standard operating conditions for calcium sulfate hemihydrate, which is present in a stable form up to 5-10%.

Note that when the plant capacity is 150 tons/day P_2O_5, only one 12-m^2 filter is used to filter the slurry.

Every 3 days, the slurry flow is switched to the other filter, and the former is washed for 24 hours.

The real rate of filtration, for comparison with similar situations, can be assumed to be about 9.4 tons P_2O_5 per m^2 of filter area per day.

This is a very high filtration rate and it points out to the satisfac tory result obtained by this plant revamping project.

It must also be stressed that the residual sludge in the settling tank after concentration can be fed back to the digestion step without any worsening effect on gypsum crystallization.

This was not possible in the "old" plant, and the sludge had to be filtered through a special filter on a batch basis.

Operating results as obtained before and after plant revamping are shown in Table 3.

Note that in the revamped plant, that is, after installing the axial- -flow pump, plant capacity went up by 25%, P_2O_5 equivalent content rose from 27.5% to 29%, and total process yield increased by 1.5%.

A study was also conducted by the Fertimont Research Center staff at Porto Marghera on the different types of surface-active agents to be used to modify the crystal structure.

Their objective was to find out a specific surface-active agent for each type of phosphate.

The study was run in the prepilot plant where phosphate rock characte rization is carried out on a routine basis (4).

The importance of the above study was fully confirmed by its results (see, for example, the pictures in Figures 6-8 showing gypsum crystals obtained from Marocco Khouribga 70 BPL phosphate).

The Montaline SP/CV non-ionic surface-active agent that had success fully performed when using Florida rock (see Figures 4 and 5), did not give equally satisfactory results with Khouribga phosphate.

Better gypsum crystals were obtained when the same type of rock was used with a different surface-active agent, i.e., SP/CV Al. As shown in Figure 8, the effect produced by this surface-active agent was quite excellent when also kieselghur was added to form fluorine com plexes with the fluorine in the SiF_6 ion and to eliminate the unfavo rable influence of fluoride ions.

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ECONOMIC EVALUATION OF PLANT ALTERATIONS

The following is an evaluation of the economic results obtained through the alterations introduced into the phosphoric acid plant only, all of the other conditions being unchanged. In other words, the savings resulting from the use of diluted H_2SO_4 and the steam produced in the ammonium nitrate reactor are not taken into account.

The major alteration consisted, as said above, in the axial-flow pump to recycle slurry, costing L. 500 million (1981 value).

Assuming the yearly output totals 50,000 tons of P_2O_5 from Florida rock phosphate, the economic review of the revamped plant performance shows the following savings:

Types of Savings	Saved Amount/yr (Lire millions)
1. Savings on phosphate rock resulting from increased process yield 2,600 tons/yr x 68,000 Lire/ton	177
2. Savings on H_2SO_4 resulting from increased process yield and lowered H_2SO_4 consumption 3,500 tons/yr x 68,000 Lire/ton	280
3. Electric power cost savings resulting from the elimination of the grinding step 2,800 Mwh/yr x 40,000 Lire/ton	140
4. Savings resulting from reducing limestone consumptions because of lower gypsum acidity 200 tons/yr x 40,000 Lire/ton	8
5. Maintenance cost savings resulting from the elimination of the grinding step	100
6. Transport cost savings on gypsum 20,000 tons/yr x 1,500 Lire/ton	30
7. Labor cost savings – one job in the grinding operation	110
8. Savings on steam for concentration 12,000 tons/yr x 40,000 Lire/ton	480
9. Electric power cost for the new axial-flow pump 400 Mwh/yr x 50,000 Lire/Mwh	- 20
TOTAL	1,305

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ECONOMIC RESULTS FROM PLANT INTEGRATION INTO THE FACTORY

By integrating the revamped plant into the factory it became possible
to use 72% instead of 99% H_2SO_4 in the phosphoric acid manufacturing
department. This means that energy cost savings can be obtained since
the reactors require only a very low degreee of cooling now.

A drawback is, however, the need for reducing the amount of water to
be used for gypsum washing, which makes it impossible to concentrate
H_3PO_4 beyond a 29% content of P_2O_5 equivalent.

On the whole, plant integration is economically advantageous, but
this is not taken into account in this report.

The utilization of steam produced in the ammonium nitrate reactors
for phosphoric acid concentration is quite a favorable side-effect.

First, it reduces the work load of the factory centralized cooling
system. In the past, the steam produced in the above reactors had
to be condensed in surface coolers. (As a matter of fact, a local
use of it is not possible because of its too low pressure)
This development has resulted in energy cost savings that are not
considered in this paper.

The most direct saving is to be seen in the amount of fresh steam to
be provided for phosphoric acid concentration, which is about 70,000
tons per year.

However, steam saving cannot be so large as it could be because the
two manufacturing units involved are not always operating simultaneou
sly, and consequently recovered steam cannot be available at any mo
ment.

Our calculation - to be confirmed over several years' operation -
indicate that steam savings should total about 55,000 tons of steam
per year, or L. 2,200 million per year.

The basic changes introduced into the steam system consisted in a
new pipeline connecting the two manufacturing units (i.e., fertili
zers and phosphoric acid manufacturing plants), and in the substitu
tion of old carbon steel shells of heat exchangers with new ones,
AISI 304 stainless steel made, in the H_3PO_4 concentration section.

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The capital investment was L. 1,500 million.

A simplified diagram of the above integrated system is shown in Fi
gure 9.

CONCLUSIONS

Feeding slurry from reactor 3 back into reactor 1, with sulfuric acid
being added through a recycling pump is the most significant change
implemented into the phosphoric acid manufacturing plant at Fertimont's
Porto Marghera facilities. By this system feature it is much easier
to control supersaturation and to optimize the rate of crystal growth
now.

A new manufacturing cycle was also developed allowing for certain
types of phosphate rock (such as Florida phosphate) to be used without
preliminary grinding. In the new manufacturing process a higher tempe
rature can be maintained, and the amount of free SO_4 is lower than in
the past.

By the new process, it is now possible to obtain gypsum containing
between 5 and 10% of calcium sulfate hemihydrate in a stable form.

Advantages over the "old" plant can be summarized as follows:

- increased overall P_2O_5 yield at the filter from 95.5 to 97.0%;
- increase in plant capacity from 120 to 150 tons/day;
- increase in the P_2O_5 concentration from 27.5 to 29.0%.

By investing about L. 500 million, L. 1,305 million can be saved eve
ry year.

In addition to that, work is in progress to create an integrated steam
system between the phosphoric acid unit and the plant where NPK is pro
duced by nitric acid treatment.
The new steam system will convey steam from the NPK unit for phospho
ric acid concentration.

When this new system (costing L. 1,500 million) becomes available, a
return on the investment of approx. L. 2,200 million per year is expec
ted.

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Table 1 - Equipment Characteristics

1. Premixers   No.   2

dimensions:	diameter	mm	3000
	total height	mm	3500
	actual capacity	m3	10 (each)
	material		Rubber-lined carbon steel

Stirrers:	type	screw-propeller, with 4 blades
	motor power	HP 8
	shaft material	Rubber-lined carbon steel
	screw-propeller material	Alloy 20

2. Reactors

			Reactor 1	Reactors 2,3,4
dimensions:	diameter	mm	4400	3400
	total height	mm	5050	5050
	actual capacity	m3	50	40 (each)
	material		Rubber-lined carbon steel	Rubber-lined carbon steel
Stirrers:	type		3-impeller stirrers	
	impeller type		curve blade, with 6 blades	
	material		Alloy 20	
	motor power		HP 30	

3. Filters

Giorgini type	No.	2
filter area	m2	12 (each)
pans per filter	No.	58
filtering sections	No.	4
pans material	AISI	316
filter cloth (Meraklon(r) polypropylene fiber cloth) threads/cm2	No.	72

4. Axial-flow pump

impeller type	3-blade screw-propeller
impeller material	Cast Hastelloy C-276
slurry delivery	m3/hr 2000
shaft material	Rubber-lined carbon steel
motor power	HP 100
absorbed power	HP 70

Table 2 - Operating Conditions

Parameters	Unit of Measure	"OLD" PLANT	"REVAMPED" PLANT
Axial-flow pump	-	NO	YES
P_2O_5 output	P_2O_5 t/d	120	150
Phosphate rock consumption	tons/ton P_2O_5	3.338	3.236
H_2SO_4 consumption	tons/ton P_2O_5	2.681	2.610
Phosphate rock grinding	-	YES	NO
Residual phosphate rock on 100 mesh sieve	%	35	60
H_2SO_4 percent. content	%	72	72
Temperatures:			
PR1	°C	78	84
PR2	°C	87	90
SA1	°C	90	95
SA2	°C	88	95
SA3	°C	86	95
on filter	°C	80	85
Digestion yield:			
PR1	%	20.0	15.5
PR2	%	60.0	20.0
SA1	%	98.5	-
SA2	%	99.0	99.6
Slurry from SA3 (as such):			
solid contents	%	34	37
after filtration:			
SO_4	%	33	27
P_2O_5	%	27.8	29.3
Filtration:			
filter speed	m/min	5.5	7.0
cake thickness	cm	5.0	6.0
rate of filtration	P_2O_5 t/m^{2}d	7.5	9.38
P_2O_5 content in produced H_3PO_4	P_2O_5 %	27.5	29.0
P_2O_5 content in last filtrate	P_2O_5 %	2.5	1.7

Table 3 - Crystal Properties, Chemical Analysis, and Yields

| Parameters	Unit of Measure	"OLD" PLANT	"REVAMPED" PLANT
1. Crystal Properties			
- Nucleation rate	$hr^{-1} \cdot 10^9$	4.5	1.5
- Growth rate	$\mu m \cdot hr^{-1}$	3.36	4.57
2. Chemical Analysis of Gypsum (on dry basic)			
- Water-soluble P_2O_5	%	0.22	0.13
- Citrate-soluble P_2O_5	%	0.56	0.45
- Insoluble P_2O_5	%	0.22	0.09
- Total P_2O_5	%	1.00	0.67
- $CaSO_4 \cdot \frac{1}{2}H_2O$	%	2.0	7.0
3. Yields			
- Attack	%	99.0	99.6
- Washing	%	99.0	99.4
- Technical yield on filter	%	95.5	97.0
- Total yield	%	94.5	96.0
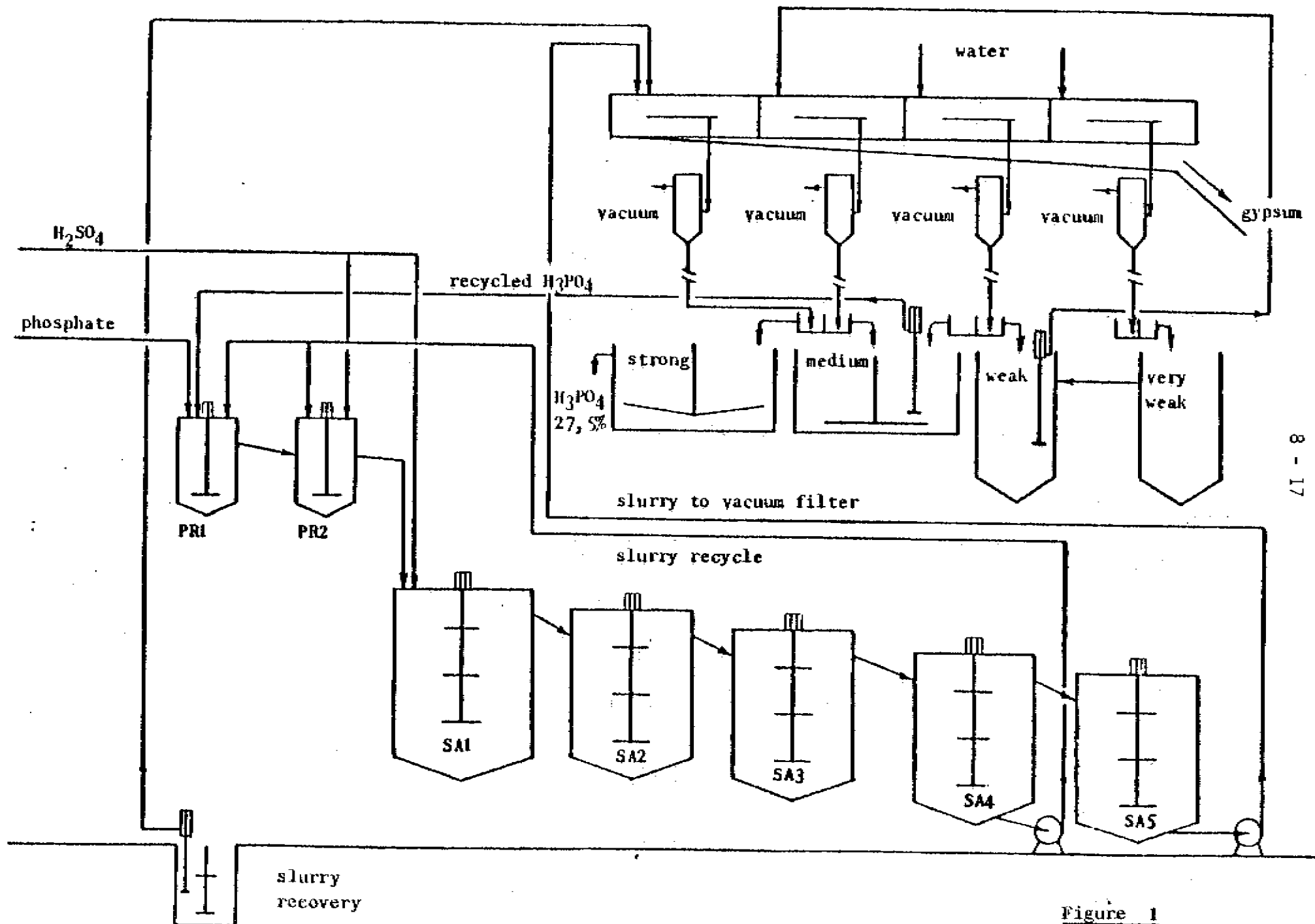
Figure 1
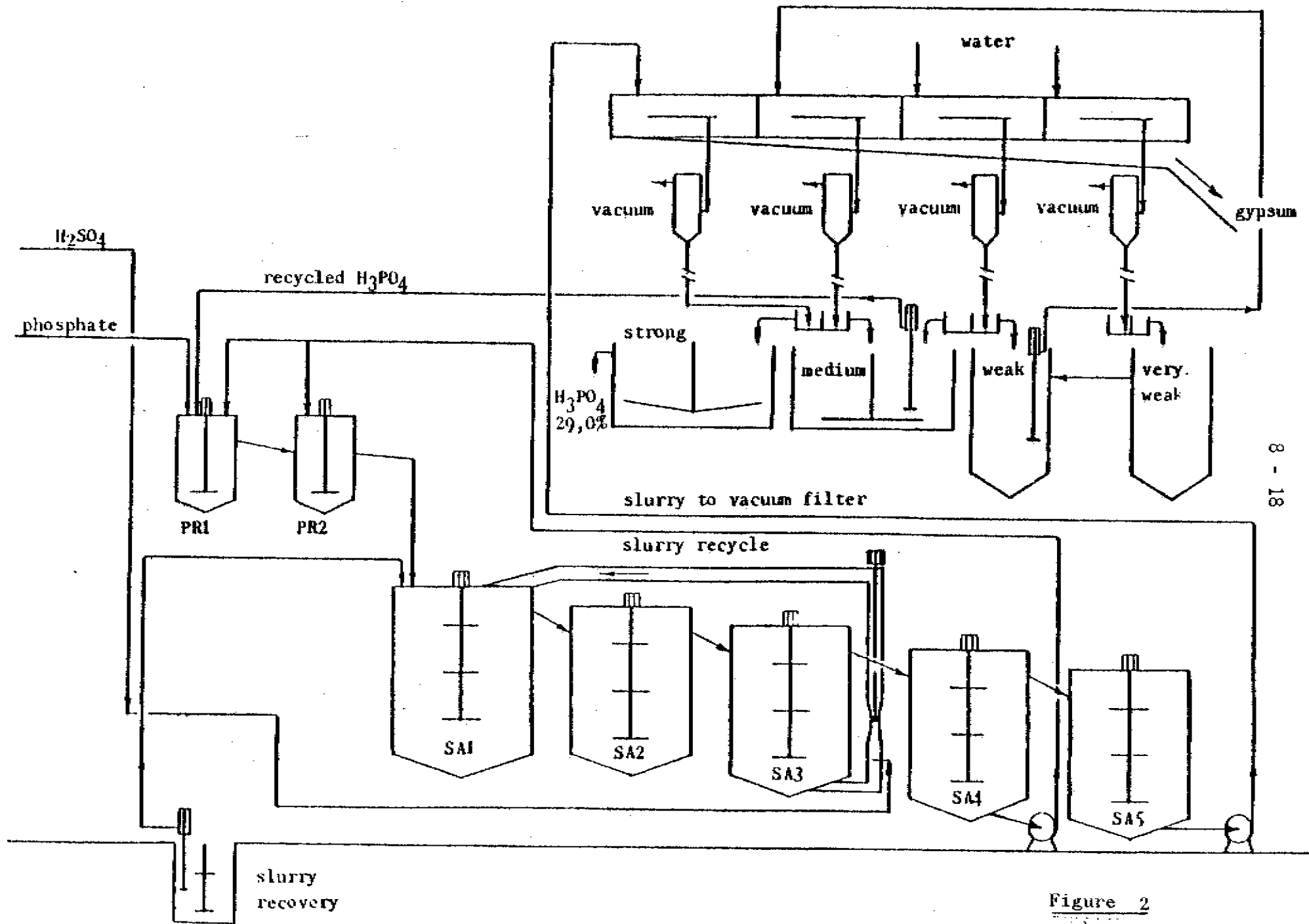
Figure 2

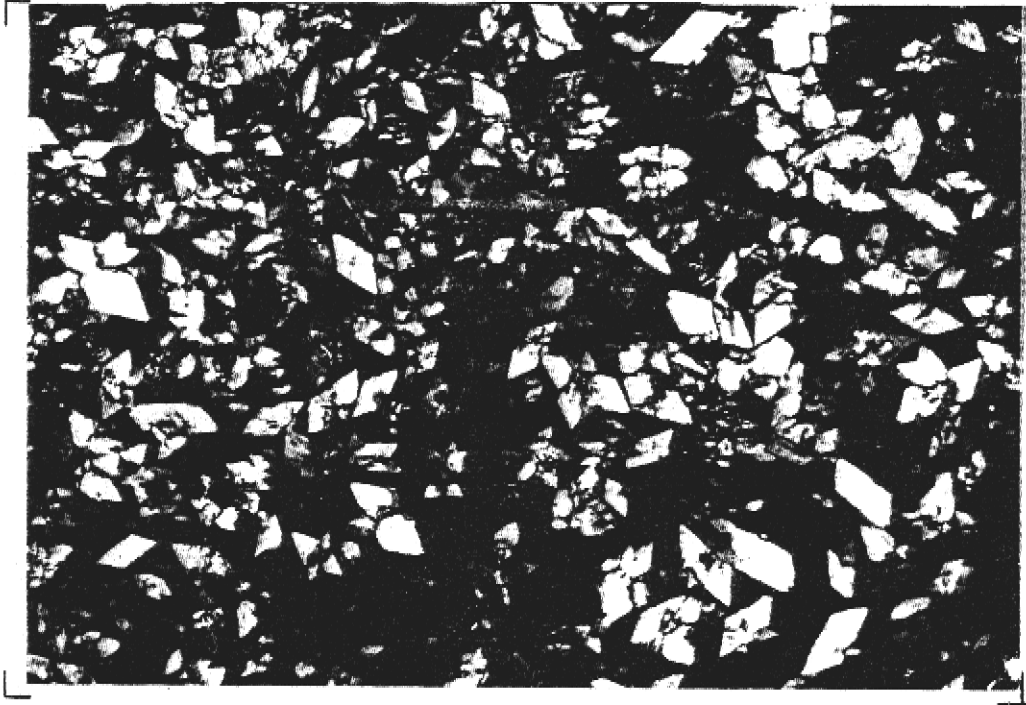## Figure 3

Axial-flow impeller
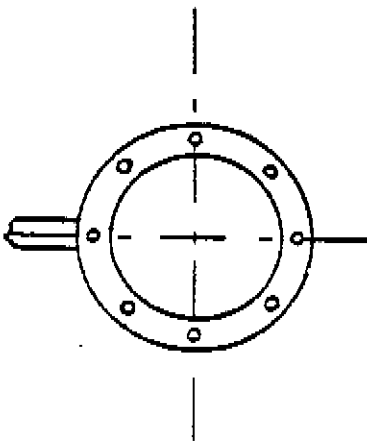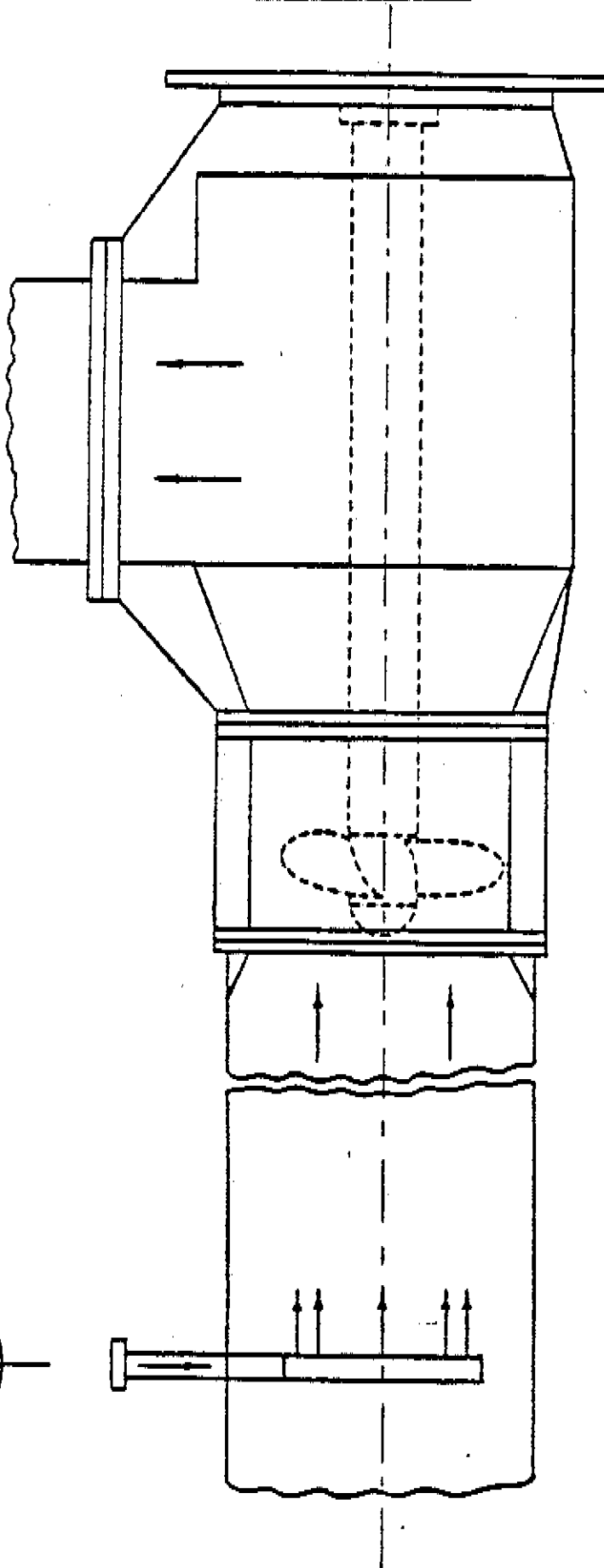
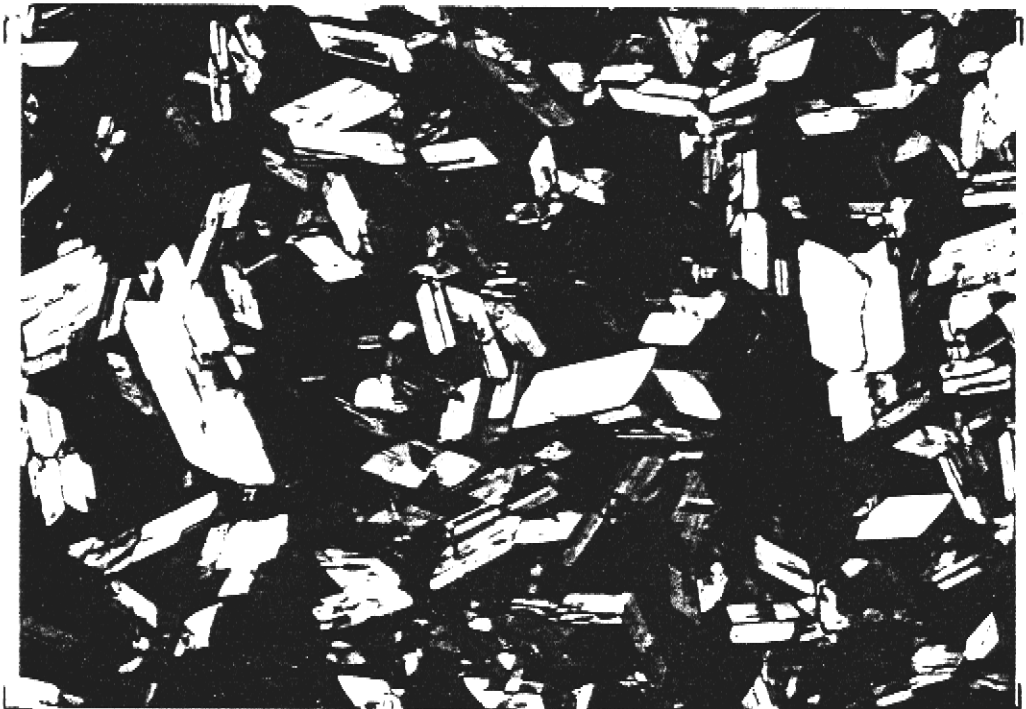Figure 4 - Gypsum crystals produced in the "old" plant
(neg. 7447)   (100x)

Figure 5 - Gypsum crystal produced in the "revamped"
(neg. 3210)   plant (100x)

Figure 6 - Gypsum crystals obtained with Montaline
(neg. 7190)   SP/CV surface-active agent (100x)

Figure 7 - Gypsum crystals obtained with Montaline
(neg. 7196)   SP/CV Al surface-active agent (100x)

Figure 8 — Gypsum crystals obtained with Montaline
(neg. 7270)   SP/CV Al surface-active agent and kiesel
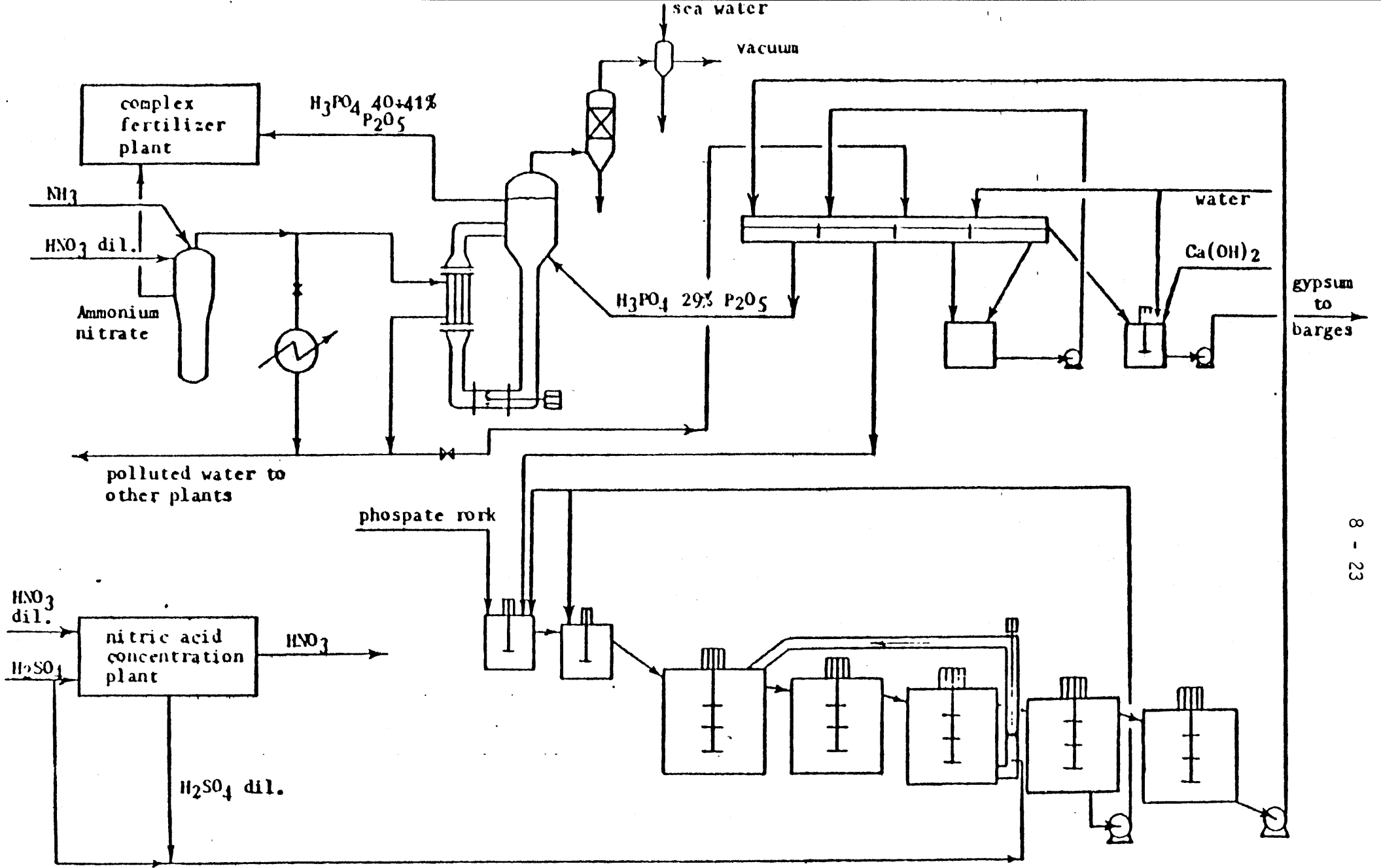guhr (100x)

Figure 9

HNO$_3$ – NPK – H$_3$PO$_4$ Plant

CONTINUOUS PHOSPHATE AND SULFATE DETERMINATION IN THE MANUFACTURE OF PHOS PHORIC ACID BY THE WET METHOD.

The determination of the sulphate ion and phosphate ion concentrations in slurries obtained by phosphate rock acidulation with sulfuric acid is quite essential to properly control the phosphate rock dissolution process and gypsum crystallization.

Traditional analytical methods, when adopted as in-process control methods, are extremely time-consuming and call for an enormous deal of repetitive work. In addition to that, their application to the particular process discussed here is not satisfactory because they involve slurry sampling and sample filtration, which causes a radical change in equilibrium conditions within the slurry, and consequently the clear filtered solution is by no means representative of the actual conditions to be found in the reactor.

Therefore, continuous sampling of the slurry, followed immediately by sample dilution to inhibit calcium phosphate settling, must be the first essential step in any analytical system for the precise determination of the sulphate and phosphate ion concentrations in the reactor.

In addition to that, the use of thermometric measures, particularly effecti ve when high ion concentrations must be determined, enable us to develop a continuous analytical system including all the analytical steps – from slurry filtration and solution sampling to result recording.

The analytical system developed by us is based on the measurement of enthal py (5) as it changes during the precipitation of phosphate ions as ammonium phosphate ions and of sulfate ions as barium chloride.

The enthalpy change is proportional to the individual ion concentration in the solution.

Sampling and sample filtration

Samples are taken from the slurry by means of a cylindrical, stainless-steel (AISI 316L) probe (internal diameter 14 mm), closed at its lower end and with 4 mm perforations (very close to one another) up to 50 mm from its lower end. (See Figure 1)

The probe is lined with filter cloth having pores measuring approx. 100x30 μm each.

A rigid-plastic sampling tube is introduced into the probe, and its end carries a reagent filter with 10 μm pores.

A stainless-steel insulating tube protects the sampling tube from the upper end of the probe to the injection fitting of the analytical instrument in order to keep the sample temperature as steady as possible and to prevent supersaturating calcium sulphate from precipitating.

After 1:10 dilution with moderately acidic water, samples are fed by a peristaltic pump to the analytical instrument for thermometric measurement.

Thermometric analysis

The enthalpy change following the precipitation of magnesium ammonium phosphate and barium sulphate is measured in flowcells developed by Technicon. Each flowcell is equipped with a magnetic stirrer operated by a small water turbine located outside the flowcell.

Flowcells have two inlets - one for the sample solution, the other for the reagent solution.

Each flowcell is closed with a metal cap to which a thermistor is coupled to record temperature changes induced by the precipitation of the ions of each substance to be assayed.

The entire analytical system is immersed in a thermostatically-controlled heating bath a. $27 \pm 0.05°C$.

The signal detected by the thermistor is sent to the amplifier, and finally plotted on a chart by the recorder.

Standard solutions and reagents

- Standard solution 28% P_2O_5 and 20 g SO_4^{--}/liter.

  Weigh 585 g of 85 %. H_3PO_4 in a 1000 ml volumetric flask, add 400 ml of a solution containing 29.57^4 g of Na_2SO_4 (anhydrous), and dilute to volume with distilled water.

- Basic solution for P_2O_5 determination.

  Dissolve 10 g of EDTA disodium salt and 15 g of NH_4Cl in approx. 800 ml of water, add 60 ml of 32 % NH_3 solution, 1.5 of wetting agent A (technicon), and dilute to 1000 ml with distilled water.

- Solution for P_2O_5 precipitation.

  Dissolve 80 g of $MgSO_4$ (anhydrous) in water and dilute to 1000 ml.

- Solution for SO_4^{--} precipitation.

  Dissolve 70 g of $BaCl_2$ in water, add 2 ml of wetting agent A, and dilute to 1000 ml.

- Diluting solution.

  Add 3.5 ml of conc. HNO_3, 1.5 ml of wetting agent A to approx. 800 ml of water, and dilute to 1000 ml with water.

Apparatus (See flow diagram in Figure 2)

The analytical system consists of the sampling probe; the peristaltic pump for sampling, reagent dilution, and dosing, the thermostated heating bath, two flowcells, the amplifier, and a two-pen recorder.

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Determination

Introduce the filter probe fitted with the sampling tube into the reactor, and start pumping the filtered sample and discarding it in a continuous way.

This maintains the sampling system temperature at the desired level, and permits continuous solution circulation within the sampling probe.

Equilibrate the analytical system, then calibrate the instrument by pumping standard solution for 5 minutes.
(See flow diagram in Figure 2)

Pump sample solution for 5 minutes every 30 minutes.
(The interval between samples is controlled by a timer-regulated valve)

Calculate the P_2O_5 and SO_4^{--} concentrations by formulas below:

$$P_2O_5 \% = \frac{\% \ P_2O_5 \ \text{std soln}}{H \ \text{of std soln}} \cdot \text{Sample H}$$

$$SO_4^- \ g/l = \frac{SO_4^- \ g/l \ \text{std soln}}{H \ \text{of std soln}} \cdot \text{Sample H}$$

where   H = Height, mm, of the peak.

Results

System reliability was tested by performing several determinations.

In each of the above determinations, 10 ml of solution was taken from the waste outlet in the analytical system (see Figure 2) and diluted to 500 ml with water. The diluted solution was essayed gravimetrically for percent. P_2O_5 content and SO_4^{--} content (as g/l).

Thermometric measurements were made immediately thereafter.

Results are compared in Table 1, and they indicate the automated analytical method described here is reliable.

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Table 1 — Comparison of results obtained by automated thermometric analysis
and a manual gravimetric method.

Sample No.	% P_2O_5 content		SO_4, g/l	
	TA	GM	TA	GM
1	28.1	28.4	17.8	18.0
2	27.0	27.0	21.0	21.1
3	26.3	26.6	20.6	20.9
4	26.5	27.1	21.5	21.8
5	28.5	28.4	13.6	13.9
6	28.9	28.3	12.9	13.2
7	28.4	27.8	19.2	19.3
8	27.8	28.1	17.7	18.0
9	27.5	27.8	19.8	20.3
10	28.0	28.1	16.8	16.8
11	28.4	28.3	19.8	20.1
12	27.5	27.9	17.9	18.4
13	29.0	29.3	18.5	18.3
14	28.7	28.8	28.6	22.4
15	28.5	28.5	20.1	20.5
16	28.5	28.4	16.9	17.0
17	28.4	27.4	14.7	14.5
18	28.4	28.4	15.7	16.0
19	28.5	28.6	19.8	20.0
20	28.8	28.6	21.3	21.4

TA = Thermometric analysis
GM = Gravimetric method

Appendix 1 - _Figure 1_

Sampling   Probe

Insulated tube

Pump 1

Filter cloth

Ø 4 mm

~ 50 mm

14 mm

Smac reagent filter
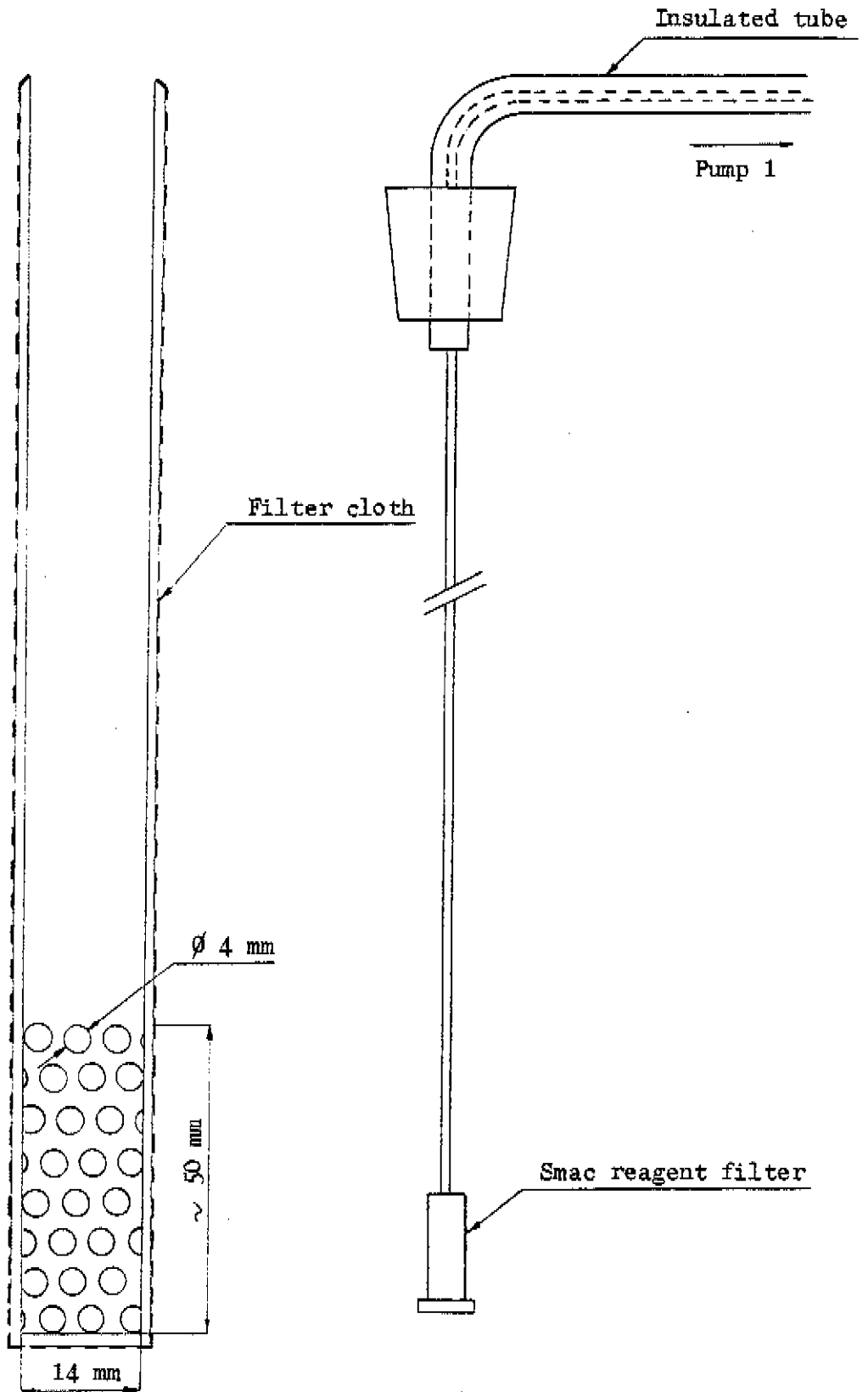
Continuous automated method for the determination of P_2O_5 and SO_4 content during the acid treatment of phosphate rock
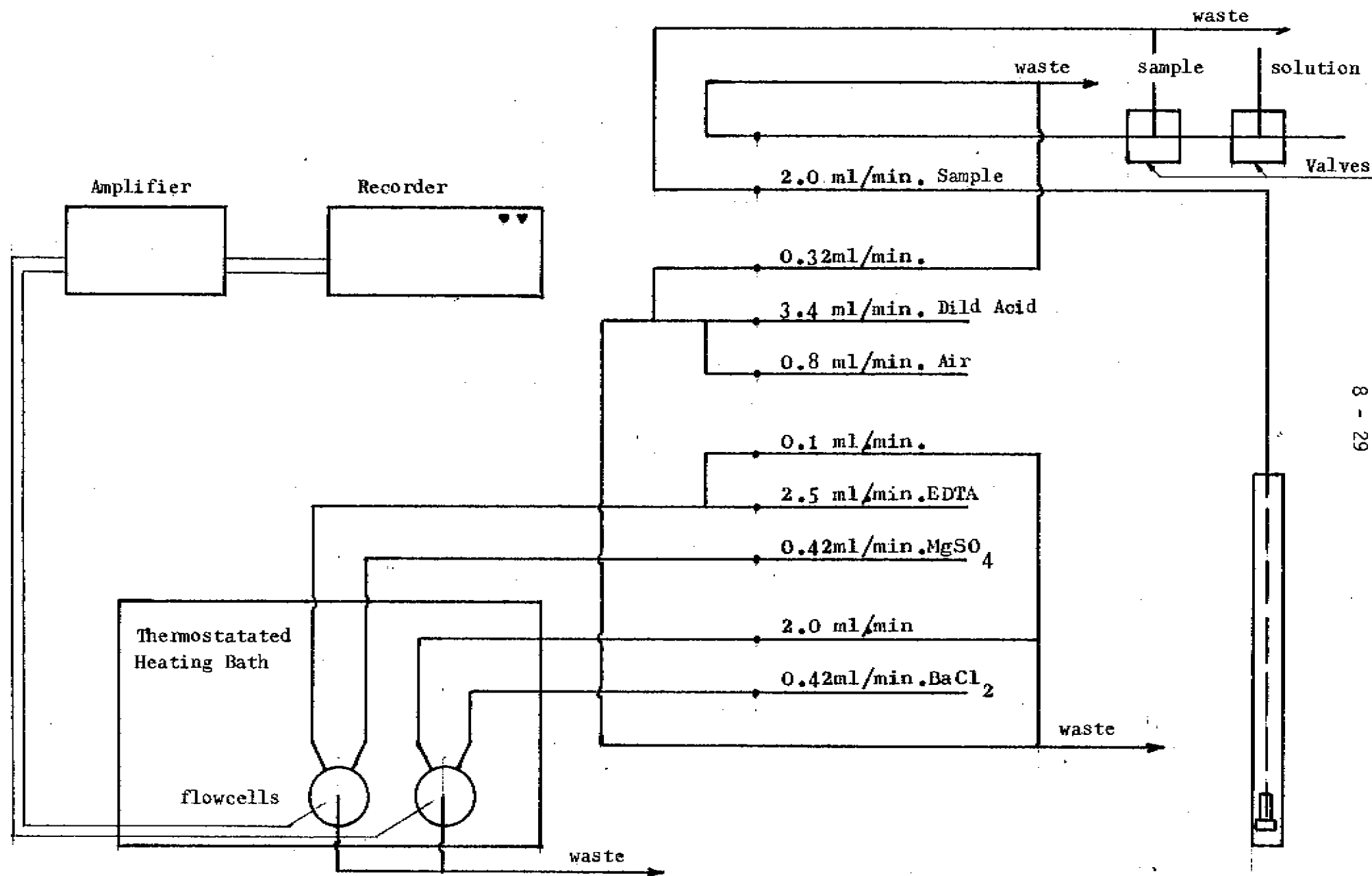
DETERMINATION OF THE RATES OF NUCLEATION AND GROWTH OF GYPSUM CRYSTALS OBTAINED DURING PHOSPHORIC ACID MANUFACTURE.

1. Scope

A method is described for the determination of the rates of nucleation and growth of gypsum crystals obtained during phosphoric acid manufactu re in our revamped plant. The revamped plant can be thought of as a continuous crystallizer where the product and the slurry can be conti nuously removed (CMSMPR).

2. Principle

On the basis of gypsum particle-size determination results, the popula tion density n is determined. Density of the population is defined here as the number of particles falling within a certain particle-size range ΔL divided by the width of the particle-size range and by the unit of volume.

The rate of crystal growth r can then be calculated from the density of the population by the equation $n = n^\circ \cdot \exp(-L/rt)$ and hence the rate of nucleation is $R_n = n^\circ \cdot r$ (1)

3. Apparatus

3.1 Series of sieves with the following opening dimensions:

212, 150, 125, 106, 90, 75, 50, 40, and 32 μm

3.2 Analytical balance, sensitivity 0.01 g.

4. Method

4.1 Particle-size analysis of the sample

Place approx. 50 g of sample on the first sieve in the above series of sieves, and shake it to effect sifting.
Collect and weigh the fractions of sample remaining on each sieve.

4.2 Determination of the crystal shape factor

The factor is determined on the largest sample fraction resulting from 4.1 above.
Apply a strip of adhesive tape (note its dimensions and weight!) onto the lower fase of the sieve immediately above the one on which the lar gest sample fraction was collected.
Transfer a certain amount of crystals to the sieve with the adhesive tape on its lower face, and shake it for a few minutes.
Remove the adhesive tape and weigh it.

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5. Result expression

5.1 Crystal shape factor

$$K_V = \frac{P - P'}{S \cdot N \cdot D \cdot \bar{L}}$$

where

P   = weight, g, of the adhesive tape + crystals remained on it
P' = weight, g, of the adhesive tape strip
S   = area, cm^2, of the adhesive tape strip
N   = number of sieve openings per cm^2
D   = density, g/cm^3, of the sample
$\bar{L}$ = Arithmetical mean of crystal size, cm (mean value of particle-sizes of crystals remained on the two sieves under 4.2)

5.2 Population density

$$n \; (cryst./\mu m \cdot 1) = \frac{100 \; G}{M \cdot D \cdot K_V \cdot \bar{L}^3 \cdot \Delta L}$$

where

G   = weight, g, of the crystals within the ΔL range
M   = weight, g, of the sample
ΔL = difference, μm, between the dimensions of the openings of the two sieves
$\bar{L}$ = mean value, cm, of the successive sieves.

5.3 Growth rate

Plot the values of ln n (5.2 above) on the y-axis and the corresponding $\bar{L}$ values on the x-axis of a diagram.

Draw the least square interpolation line between successive points.

The growth rate is equal to

$$r \; (\mu m/hr) = - \frac{1}{b \cdot T}$$

where

b   = slope of the line
T   = crystal residence time, hrs.

5.4 Nucleation rate

$$R_n \; (nuclei/hr) = n^o \cdot r$$

where

n^o = density of the crystal population as determined by the intercept of the line drawn under 5.3 above with the y-axis

$$a = \ln n^o$$

An example of the graph is shown in Figure 1.

6. Conclusions

The above method was tested for reproducibility on 5 samples of one type of gypsum.

Data, as shown in Table 1, are of a good quality.

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The method can then be viewed as reliable for studying and/or controll ing gypsum crystallization kinetics in our phosphoric acid manufactur ing unit, which is extremely useful because kinetic data are very im portant for efficient plant operation.

Kinetic data can also be used to determine other parameters, such as mean crystal size (L_D), total crystal mass (W_T), and the total crystal number per unit of volume (N_T):

$$L_D \text{ (um)} = 3 \cdot r \cdot T$$

$$W_T \text{ (g/l)} = 6 \cdot K_v \cdot D \cdot n^o \cdot (rT)^4$$

$$N_T \text{ (cryst./l)} = n^o \cdot r \cdot T$$

Table 1 – Rates of nucleation and growth, standard deviation (S.D.), and percent. variation coefficient (P.V.C.)

|	Mean Value	S.D.	P.V.C.
r (um/hr)	6.52	0.21	3.22
R_n (nuclei/hr)	$2.26 \cdot 10^8$	$0.16 \cdot 10^8$	7.08

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Appendix 2

Figure 1

Example of a chart for the determinations of the nucleation rate and growth of gypsum crystals

ln n°

Nucleation rate $R_n = 3 \cdot 4 \cdot 10^8$ nuclei/h

Growth rate $r = 6,9$ m/h

Sieve openings

$\breve{L}$
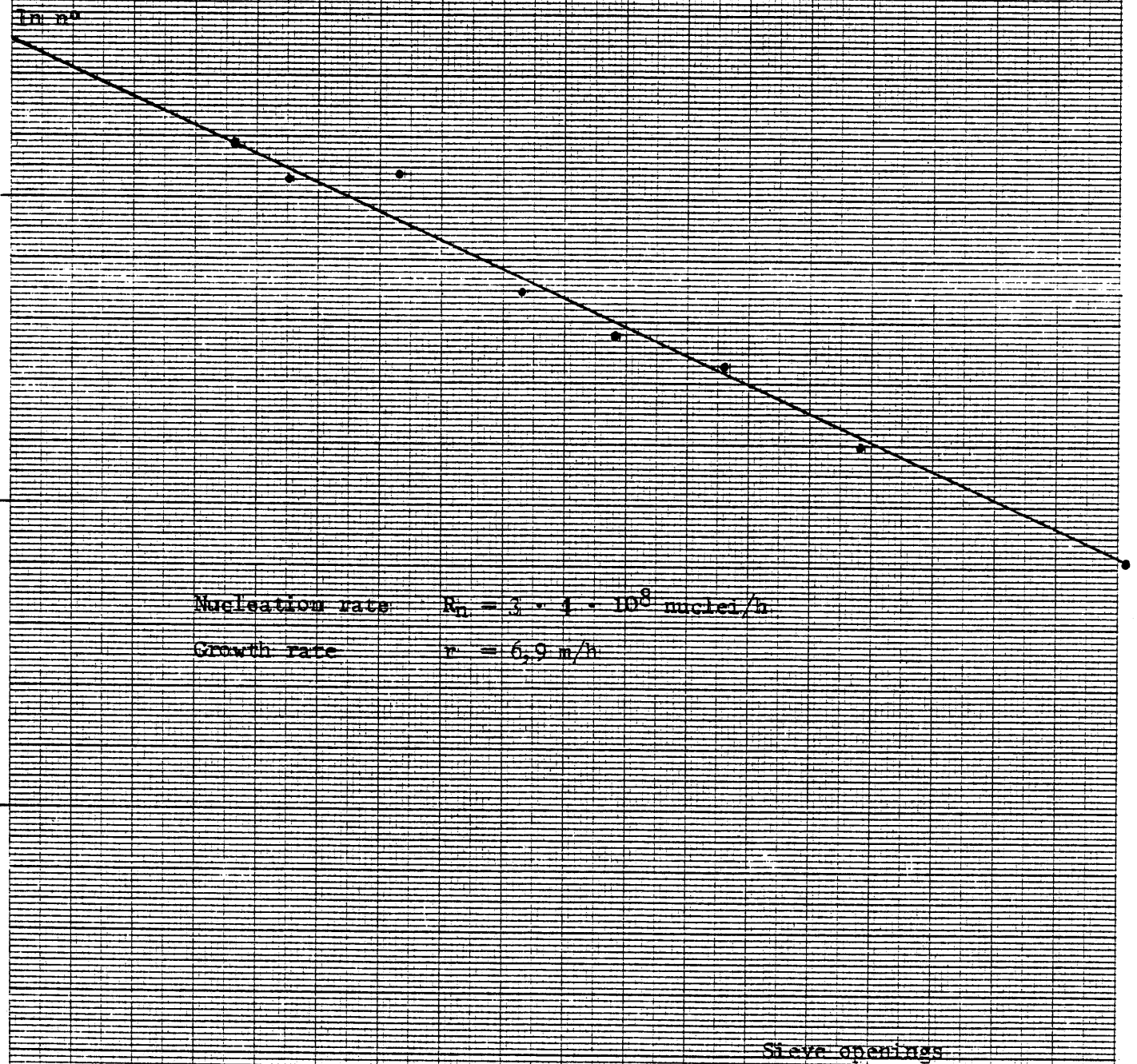
TA/82/8 Revamping and energy cost reduction obtained in one of Montedison's phosphoric acid plants with low investment cost, by R. MONALDI, A. BARBERA, F. SOCCI and G. VENTURINO, Fertimont SpA, Italy

(DISCUSSION : Rapporteur Mr. J.H. Markham, ICI Ltd, United Kingdom)

Q - Mr. J.Th. BOONTJE, UKF, Netherlands

a) In Literature the most powerful crystal habit modifying action is attributed to the combination of Al and F in the acid. In our experience it is not the optimum to convert all the F by SiO_2 into H_2SiF_6 because this causes growth of elongated crystals with no optimal filtering properties. Bentonite or Kieselguhr also bring aluminium into solution which influences crystal growth. Have you other ideas about these mechanisms?

b) What is the advantage to have 5-10% hemihydrate in the dihydrate? (Page 8-13)

A - a) At the Research Centre some work was carried out on the effect of other impurities. This demonstrated that the important effect was the combination of SiO_2 with F. The work also showed that Florida and Togo phosphate rocks do not require any additional SiO_2.

b) The hemihydrate presence is not an advantage - simply a result of increased temperature in the reactor.

Q - Mr. J.D. LOGEMANN, DSM, Netherlands

Regarding influence of gypsum crystal growth by fluoride ions.

Did you obtain quantitative data on growth rate and nucleation rate as a function of fluorine concentration?

A - So far there are only results of the laboratory trials with nothing from the industrial trial. The speaker agreed to provide data to Mr. Logemann when it became available.

Q - Mr. P. SMITH, QUIMBRASIL, Brazil

a) Was the use of surface active agents fully optimized on the old plant and does Fig. 4 of your paper apply to crystals produced using surface active agents?

b) Have you considered modifying the Giorgini filter to a belt filter type? If not what are the advantages of the Giorgini filter?

A - a) The crystals on the old plant Fig. 4 were produced with the use of the surface active agent and can be compared with those produced on the revamped plant as shown in Fig. 5.

b) The Giorgini filters perform very well and we have had no reason to consider modifying them.

Q - Mr. J.M. ENRIQUEZ, Davy McKee, USA

a) What is the total CaO and SO_3 in the liquid phase of PR2?

b) Have you tried to use your analyser in places where the CaO in the liquid phase exceeds the SO_3? Do you still find good correlations with gravimetric determinations?

A - a) No measurements have been taken.

   b) No measurements have been attempted at any places other than where gypsum crystallization occurs.

Q - Mr. P. BECKER, COFAZ SA, France

   a) According to literature and also your paper, the crystal growth rate versus crystal size is constant in a given medium. We have found that the growth rate is smaller for the 0-30 micron sized crystals (in the case of phosphoric acid production). What is your experience?

   b) How do you express ΔC supersaturation - units?

   c) Can you explain with more detail the determination of the crystal shape factor?

A - a) No further comments.

   b) The units are gms/litre SO_4.

   c) This test is not very accurate. It is described in the paper in detail. It does not describe the true shape of the crystals.