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CRYSTALLIZATION AND CO-CRYSTALLIZATION

IN THE MANUFACTURE OF

WET-PROCESS PHOSPHORIC ACID.

By J. Fröchon & P. Becker,
Societe Industrielle d'Acide
Phosphorique & d'Engrais.

INTRODUCTION

An analysis of losses during the manufacture of phosphoric acid by the wet process has led us to give very special attention to P_2O_5 losses which could not be leached out but which did not come from unreacted phosphate rock.

This paper presents in part one the work we undertook to determine the nature of these losses and our study of the factors responsible for variations.

The second part describes the correspondence we established between these losses and the type of crystallization obtained.

The third part attempts to explain the observed facts.

P_2O_5 LOSSES IN THE GYPSUM

We studied our P_2O_5 losses during the manufacture of phosphoric acid by the wet process and we were able to classify them under three heads:

- 1) losses in the form of phosphoric acid
- 2) losses in the form of unreacted rock
- 3) losses of P_2O_5 incorporated into the actual gypsum crystals
(not leachable)

The phosphoric acid losses are due to the acid impregnating the gypsum crystals and failing to be washed out on the filter. The amount of these losses is therefore governed by the type of crystallization, the number of washes and the type of filter. This is the first loss to be considered by the phosphoric acid manufacturer because, although it is generally small, if the plant is not running properly, it can easily reach quite high levels. Usually it amounts to about 1 to 2% of the P_2O_5 in the system.

The losses in the unreacted rock are caused by particles of rock becoming coated with gypsum which protects them from attack by the acid. Usually, this is a very small loss and the plant had to be run in a particular way, as we shall see later, for this loss to become significant.

There remains the P_2O_5 contained in the actual gypsum crystals. We have established that this type of loss is responsible for by far the greatest proportion of the losses. In our plant, it represents about 4% of the P_2O_5 in the system. Other samples we have analysed have shown that this percentage may vary between 2 and 4.5 according to the works supplying the sample. The results vary between one works and another but they are remarkably consistent for each works. The size of this loss induced us to direct our research effort first towards finding the nature of this P_2O_5 contained in the gypsum.

NATURE OF THE P_2O_5 IN THE GYPSUM

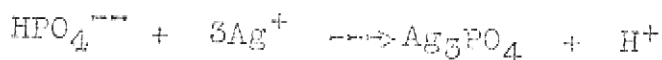
The literature (see Appendix I) shows that some authors suppose that the gypsum crystals obtained during the manufacture of wet-process phosphoric acid are impure and that a certain number of HPO_4^{--} ions co-crystallize (i.e. displace SO_4^{--} ions) in the crystal lattice.

But this is by no means proved. We therefore re-examined the problem and with a sample of gypsum whose preparation we will describe below we carried out a series of tests which we hoped would reveal the exact nature of this compound. The high P_2O_5 content of this gypsum helped this investigation.

Presence of the H^+ ion

To confirm the presence of HPO_4^{--} ions, all that we required was to show that the hydrogen atom was present and then to determine the relative amounts of this and P_2O_5 , which we did by substituting silver for this atom.

For this purpose we placed 2 g of gypsum containing 5.4% P_2O_5 in a litre of deionised distilled water and shook it until completely dissolved. To 200 ml of this solution we added a 3N solution of silver nitrate in the presence of the electrodes of a pH-motor. The silver nitrate solution caused a rapid fall in the pH of the solution due to the liberation of H^+ ions by the following reaction:



So as to make certain, we carried out the same test with a gypsum containing 3.6% P_2O_5 prepared with pure reagents and with a chemically pure gypsum, free from P_2O_5 , which was our control.

X-ray results (C.P.A.N.)

When we look at the X-ray results, we are struck by the number of properties common to both gypsum and dicalcium phosphate:

crystal structure
no. of molecules of water of crystallization
molecular weight
density
ionic structure

The figures for gypsum and dicalcium phosphate are thus very similar, although certain characteristic lines enable us to tell one from the other. We compared the figures for pure gypsum, pure dicalcium phosphate (brushite) and the 5.4% P_2O_5 sample. This comparison showed:

- 1) that the 5.4% sample does not contain the lines which are characteristic of brushite
- 2) that the figure for pure gypsum is reproduced almost exactly (some lines are slightly displaced or are slightly less intense)

which leads us to the conclusion that the dicalcium phosphate is not present in the pure form but that the HPO_4^{2-} ions have displaced the SO_4^{2-} ions, thus slightly modifying the figure for pure gypsum. It should also be mentioned that the line characteristic of ardealite ($Ca_2HPO_4SO_4 \cdot 4H_2O$) was not found, which cuts out the possibility of an admixture of this substance with the gypsum.

Conclusion from the quantitative tests.

This series of tests certainly confirms that only one phase is present and that there is in fact a displacement of the SO_4^{2-} ion by the HPO_4^{2-} ion in the crystal lattice.

FACTORS INFLUENCING THE P_2O_5 CONTENT OF THE GYPSUM

Now that we know the form in which the P_2O_5 was incorporated in the gypsum, we set out to find what factors influenced its P_2O_5 content. For this purpose we tried to reproduce plant conditions in the laboratory and studied the influence of different factors on the P_2O_5 content of the gypsum, while keeping within the limits of normal working conditions. To this end we used a reactor vessel first to identify and subsequently to study within the range of normal working conditions of a phosphoric acid plant, each of the factors which influences the P_2O_5 content of the gypsum.

Apparatus

We made a scale model of the reactor vessel. For this we used a stainless steel cylindrical vessel, holding 8 litres, fitted with an agitator with 4 blades each 55 x 28mm and a speed of 300 rpm.

Sulphuric acid and rock were fed in continuously, as during manufacture.

in relation to

Figure 1 shows the three potentiometer curves as a function of the volume of silver nitrate added. The low acidity shown in the pure gypsum sample is due to the silver nitrate which must be slightly acid so that it will not precipitate silver hydroxide. We titrated the acidity with NaOH of known strength and from this we calculated the H^+/P_2O_5 ratio which was in both cases exactly $2H^+ : 1P_2O_5$. This confirms the presence of the dicalcium form.

It now remained to be seen whether we were dealing with a single phase or whether we had a mixture of crystals. We therefore determined by three different methods (X-ray, thermobalance and thermo-differential analysis) the properties of the gypsum with 5.4% P_2O_5 , pure gypsum, pure dicalcium phosphate and finally a mixture of the two last in the appropriate ratio.

Thermobalance results (C.P.A.N.)

We did this test with:

- 1) the 5.4% sample
- 2) pure gypsum
- 3) pure dicalcium phosphate
- 4) a mixture of crystals of: 88% $CaSO_4 \cdot 2H_2O$
12% $CaHPO_4 \cdot 2H_2O$ (=5% P_2O_5)

The figure obtained with the crystal mixture has no points in common with the 5.4% sample, which gives the same figure as pure gypsum. The mixed crystal sample clearly shows the properties of both gypsum and dicalcium phosphate (fig. 2 & 3).

Thermo-differential results (C.P.A.N.)

We tested the same samples and the figures obtained gave the following properties:

<u>Gypsum with 5.4% P_2O_5</u>	115-225° endothermic loop (water loss) 700° exothermic point (far) 975° exothermic wave (decomposition)
<u>Pure gypsum</u>	115-235° water loss 850° decomposition
<u>Pure $CaHPO_4$</u>	70-165° water loss 310° exothermic point 310-510° decomposition to pyrophosphate 985° endothermic reaction
<u>Crystal Mixture</u>	shows simultaneously the properties of gypsum and dicalcium phosphate 90-245° loss of water of crystallization 350° exothermic wave 875° endothermic loop

(see fig.4)

Here again we see that the 5.4% gypsum does not behave like the two-phase mixture but like the pure material. Its figure is exactly the same as that of gypsum, except for the far exothermic point which is not shown on the figure.

During these trials we made volumetric determinations of the concentrations, so as to avoid any unwanted effects due to irregularities. Thus, the sulphuric acid excess is expressed as acidity and should not be confused with the SO_4^{--} concentration which is higher owing to the presence of sulphates.

The rock used was 65% Gafsa ground to pass 75% through a 100 screen and containing 29.4% P_2O_5 .

1) Influence of sulphuric acid excess.

This factor was mentioned by Waggaman (see Appdx I). He stated that the sulphuric acid concentration affects the P_2O_5 content in the gypsum. This can easily be explained. The crystals are formed from Ca^{++} and SO_4^{--} and these attract a certain amount of HPO_4^{--} in a statistically constant ratio. As the SO_4^{--} concentration increases, the Ca^{++} concentration falls (solubility product) while the HPO_4^{--} ion concentration also falls owing to the presence of the sulphuric acid which is a strongly dissociated acid. Consequently, we may expect that the HPO_4^{--} content of the crystal lattice of the gypsum will decline in the presence of an excess of sulphuric acid.

In order to estimate the quantitative effect of this factor, we carried out several reactions varying the excess of sulphuric acid. For each trial we took 4 litres of pure phosphoric acid saturated with calcium sulphate and seeded with 0.5 g/litre of crystals. Unlike the previous trials, these were carried out with pure phosphoric acid so as to be able to make a precise volumetric measurement of the excess of sulphuric acid. Of course, with the acid made under plant conditions, the volumetric results are greatly affected by the iron and aluminium salts present.

These trials were carried out with an excess of sulphuric acid of 0, +10, +20 and +30 g/litre respectively. In each trial we reacted 50 g rock at the rate of 10 g per minute.

Trial No.	Acid Excess	Acid Volume	Temp.	Attack Rate	Phos. Acid conc.
1	+ 0 gr/lit.	4 L	70°	10 grs/min.	340 grs/l
2	+ 10	4 L	70°	- " -	- " -
3	+ 20	4 L	70°	- " -	- " -
4	+ 30	4 L	70°	- " -	- " -

Results are shown in fig. 5 which shows clearly how the P_2O_5 in the gypsum declines very rapidly in proportion to the growing excess of sulphuric acid.

The gypsum obtained in these trials contains fairly large amounts of P_2O_5 . This is due to the fact that we used very little rock for each trial and hence the percentage of crystals in the slurry remained low. Now, as we shall show, this increases the P_2O_5 content in the gypsum in these 4 trials. Nevertheless, the graph is a true picture of the relative variation caused by an excess of sulphuric acid.

2) Influence of the percentage of crystals in the slurry and of the strength in P_2O_5 of the phosphoric acid.

The influence of the acid strength is already known (Waggaman, see Appdx I). But the influence of the percentage of solid in the slurry has not previously attracted attention. This may be because this factor is not so liable to significant variations and its effects are less intense within the range normally employed.

When gypsum is precipitated by feeding in simultaneously and continuously rock and sulphuric acid into a filtered solution of phosphoric acid, we have initially a liquid medium which becomes progressively richer in solid particles in suspension.

At the beginning of this operation, all the calcium sulphate formed is of necessity in the form of crystal seeds; later, the SO_4^{--} and Ca^{++} ions may either enlarge an existing seed or commence a new one. When the first seeds have appeared, the total surface which may be used for the enlargement of the existing solid phase is still small, and the average distance to be covered is still large. But as the number of seeds increases, the surface grows larger and the average distance to be covered grows smaller. Consequently, the proportion of calcium sulphate enlarging the existing crystals will be greater.

Thus, we must expect to find different conditions governing the precipitation according to the proportion of solid phase in suspension, because of the difference in the mechanism of the formation of seeds and the enlargement of crystals. Accordingly, we were expecting to find side by side different P_2O_5 contents in the precipitated gypsum. Thus, in the course of these trials, we formed a slurry starting from filtered acid to which we had added, in the usual reaction method, rock and sulphuric acid. We maintained the strength of the phosphoric acid at the same level by simultaneous addition of water. This meant that the variation was in the percentage by volume of gypsum crystals in suspension.

Trials carried out with phosphoric acid of different strengths show at the same time the influence of the phosphoric acid concentration.

Procedure

During these trials we thickened slurries from 0 to 10% by volume of solid phase. At regular intervals, we took samples of the gypsum and analysed the P_2O_5 content.

In this way, we effected three reactions with 100, 200 and 340 g/l of P_2O_5 .

Trial No.	Excess Sulph. Acid.	Initial volume of acid.	Temp.	Attack Rate	Conc. Phos. Acid.	Crystals %
1	+ 0	4 L	70°	10 gr/min	100gr/l.	0 - 10%
2	+ 0	4 L	70°	- " -	200 gr/l.	- " -
3	+ 0	4 L	70°	- " -	340gr/l.	- " -

(Quantity of rock used for each trial: 1 kilogram)

Results: The samples of gypsum taken during each trial were analysed and their P_2O_5 content as a function of the rising percentage of gypsum is shown in fig. 6 for 100, 200 and 300 g/l respectively. However, the samples taken in this way correspond to the average amount of gypsum precipitated since the start of the trial and not to the fraction being formed at the time when the sample is taken.

Consequently we had to use the curves shown in Fig. 6 and a mathematical formula (explained in Appdx II) to obtain the curves shown in Fig. 7 which represent the actual P_2O_5 content of the gypsum as a function of the percentage of crystals in suspension. These curves show that the formation of seeds attracts much more P_2O_5 than the enlargement of existing crystals. As the slurry thickens, the influence of this factor falls off steeply.

It would be difficult to find a reliable explanation for this phenomenon. We would mention, however, that the formation of seeds requires a higher degree of supersaturation than the enlargement.

Therefore, in the course of these experiments, we have at the same time determined the concentration of Ca^{++} ions in solution. This determination requires a certain amount of care because it is a matter of measuring ions in a supersaturated solution, i.e., at an unstable concentration. The samples must be filtered very quickly and even in this short time a slight error will be unavoidable. We obtained the curves shown in Figure 8.

These curves, in the form $Ca^{++} = \frac{K}{\frac{n}{V \cdot G}}$, are curiously like those

which represent the behaviour of the P_2O_5 in the gypsum. Can we say that the supersaturation which is a function of the percentage of crystals in suspension is the real factor which governs the P_2O_5 content in the gypsum? For the time being, it is safer to note the resemblance without drawing conclusions.

3) Influence of the strength of the phosphoric acid:

The three curves in Fig.7. simultaneously show the influence of the strength of the phosphoric acid. In fact, between 100 and 340 g/litre the P_2O_5 content in the gypsum is proportionate to the acid concentration, whatever the percentage of gypsum in suspension.

4) Influence of the attack rate.

The study of the previous factor revealed the possible influence of the supersaturation. We therefore considered another factor affecting the supersaturation: the attack rate. By attack rate we mean the relationship:

$$\frac{\text{Food Rate} \times \text{Yield from attack}}{\text{Volume of reactor vessel} \times \text{Time}}$$

which expressed in another way represents the input of Ca^{++} and SO_4^{--} ions into a given volume of slurry.

Now, when the feed rate of acid and rock is increased, the quantity of calcium sulphate precipitated for a given volume is also greater. Since all the other factors are constant - volume of vessel, percentage gypsum in suspension, etc., - then the quantity of ions in solution must increase, because they constitute the means of transport between the starting materials, rock and acid, and the reaction product, gypsum. This appears as a higher degree of supersaturation which will accelerate the speed of crystallization by forming more seeds, as this will reduce the average distance and enlarge the active surface.

When the reactor vessel is fed with a substantial amount of recycled slurry, the influence of the attack rate will be less marked on the supersaturation because of the removal of the supersaturated slurry (active) and its replacement by saturated slurry (non-active).

It may incidentally be considered that a well-judged recycle is an artificial enlargement of the volume of the reactor vessel to the extent of the number of times the volume of the vessel can be contained in the recycled material.

We conducted two parallel trials with different rates:

Trial No.	Rate	Temp.	P_2O_5	Rock Feed	H_2SO_4 excess	Initial Vol. Acid
1	5 gr/l/min.	70°	340 gr/l.	100 gr.	0	4 litres no solid phase
2	0,415 gr/l./min	70°	340 gr./l.	100 gr.	0	4 litres no solid phase

For trial No. 1. (5gt/litre/minute) we found 1.44% P_2O_5 in the gypsum and for trial No. 2. (0.415 g/l/min) 1.34%.

There is thus some influence; although very little since the attack rate was 12 times greater in trial No. 1. It should be noted that in the slow trial the crystals are larger.

The acid with which we started contained no gypsum; consequently, we were working with a low percentage of solid phase which explains the high content of P_2O_5 in the gypsum in both cases.

5) Influence of Temperature.

Hill & Hondricks (see Appdx II) had mentioned the influence of temperature.

We carried out several reactions at temperatures varying from 50 to 100°C.

So as to cut out the influence of gypsum present in the starting acid, we once again began the precipitation with phosphoric acid free from crystals. Hence, the percentage of solid for each trial varied from 0 to 9% and thus the results are unavoidably influenced by this factor.

We thus conducted four parallel trials at different temperatures:

Trial No.	Temp.	Acid conc.	H ₂ SO ₄ excess	Volume acid	Attack rate	Rock	Phase
1	50°	340	0	4 lit.	10gr/4 l	800 gr.	gypsum
2	70°	340	0	4 lit.	"-	800 gr.	gypsum
3	80°	340	0	4 lit.	"-	800 gr.	hemi-hydrate + gypsum
4	100°	340	0	4 lit.	"-	800 gr.	hemi hydrate

At the end of each trial we analysed the average gypsum resulting from each operation, and we were able to draw up the following table:

50°	1.64%	gypsum P_2O_5
70°	1.13	"
80°	1.00	"
100°	0.88	"

Thus, the influence of temperature is considerable. At 100° we precipitated some hemi-hydrate which also contained some P_2O_5 in its crystals.

Here again, the influence of the percentage of solid in suspension, varying from 0 to about 9% in each trial, raises the values above what they would be where precipitation was continuous and the percentage of solid maintained constant at a value of, say, 20%.

We carried out another series of trials where the temperature variation was studied with the variation of the percentage solid in suspension. Starting with 2 litres of filtered acid, we let it thicken progressively up to 20% solid. We conducted three trials with temperatures of 50°, 65° and 80°. At regular intervals, we analysed the co-crystallized P₂O₅ contained in the average gypsum.

Trial No.	Temp.	Initial Volume	Excess H ₂ SO ₄	Attack Rate	Total Rock	Phase at end	Conc. P ₂ O ₅
1	50°	2 lit.	0	10 gr/21 min.	1250 gr.	gypsum	350
2	65°	2 lit.	0	- " -	1250 gr.	gypsum	350
3	80°	2 lit.	0	- " -	1250 gr.	hemi-hydr. + gypsum	350

The results are shown in Fig. 9, where we see once more the curves which are characteristic of the variable percentage of solid. The influence of the temperature is confirmed.

At the same time we controlled the crystalline nature of the precipitate. Thus, at 80° we finished up with 75% of hemi-hydrate. At the beginning of the same trial, with 5% precipitated solid, this figure was 89%.

Similarly, at 65° with 5% precipitated solid we had 40% hemi-hydrate, while at the end of the trial there was nothing but gypsum. Thus, the formation of the hemi-hydrate seems to depend not only upon the temperature and the concentration of the acids present, but also on the extent of the surface of the existing precipitate in relation to the input of reagents into the slurry. Even at 50°, the samples taken at the beginning of the trial contained some hemi-hydrate.

6) Influence of interfering ions

The influence of interfering ions on the crystal facies of gypsum is well known. Ions, particularly when they are polyvalent, such as Fe⁺⁺⁺ and Al⁺⁺⁺, cause significant variations when they are in the presence of precipitants. (Prof. Forestier has worked on this, see Appdx I). Thus, their influence might affect the P₂O₅ content of the crystals.

We examined the influence of Fe⁺⁺⁺ ions only.

For this, we dissolved 32 gr. of iron in the 4 litres of phosphoric acid before reacting it. We also ran a control trial.

Trial No.	Added Fe ⁺⁺⁺	P ₂ O ₅	Initial vol. acid	Temp.	Attack rate	Rock	H ₂ SO ₄ excess
1	8 gr/l.	340	4 l.	70°	10 gr/l. minute	80 gr.	0
2	none	340	"	70°	"	80 gr.	0

The trial with the iron gave us gypsum with 2.63% P_2O_5 , the trial without iron, 1.81%. Thus it has a considerable influence.

The presence of Fe^{+++} ions may act in two ways:

- a) Fe^{+++} ions may be absorbed on certain faces of the crystals, making them unfavourable to the passage of certain ions from the liquid to the solid phase, which would explain the influence we found;
- b) Fe^{+++} ions in solution must displace H^+ ions and consequently favour the presence of HPO_4^{--} ions.

The Fe^{+++} ion does not enter the crystal; we confirmed that it was not there.

Table showing all the factors influencing co-crystallization

Nature of factor	Variation of factor	Variation of P_2O_5 content of crystal
P_2O_5 conc. of acid	↗	↗
H_2SO_4 conc.	↗	↘
% solid in suspension	↗	↘
Attack rate	↗	↗
Temperature	↗	↘
Interfering ions	↗	↗

Thanks to a knowledge of these factors, we were able to prepare our sample with 5.4% P_2O_5 by crude precipitation, in the cold starting from a solution of monocalcium phosphate and removing the first fractions of precipitated solids:

RELATIONSHIP BETWEEN LOSSES OF P_2O_5 BY CO-CRYSTALLIZATION
AND QUALITY OF CRYSTALLIZATION

On the industrial scale, the loss of P_2O_5 by co-crystallization is significant. In practice, in the manufacture of 1,000 kg of P_2O_5 from Gafsa rock, a loss of 1% of the P_2O_5 supplied in the raw materials would amount to an extra consumption of:

45 kg rock
23 kg sulphuric acid (100%)

But this is not all. In the course of the investigation described above, we were able to confirm that all the factors whose influence on co-crystallization we established also affect the quality of the crystallization, and hence directly influence the production capacity of the manufacturing plant and consequently its output.

Factors affecting the quality of the crystallization

1) Concentration of the acid in P_2O_5

It is well known that when the concentration of the phosphoric acid is increased, other things being equal, the size of the crystals is reduced.

The reduction in the speed of the filtration which results from this is, moreover, aggravated by the increase in the viscosity of the acid due to its higher concentration.

2) Concentration of the acid in SO_4

The influence of an excess of sulphuric acid in the reaction slurry on the crystal face is equally well known.

When the Ca^{++}/SO_4^{--} ratio is near unity (stoichiometric ratio), the crystals are usually of irregular shape and crystallization occurs around a particle of phosphate rock which becomes covered with excrescences of gypsum; the appearance of the whole crystal is characteristic and resembles a spiked club.

As the sulphuric acid content is increased, lamellar crystals of gypsum begin to appear, independently of the phosphate rock particles, and these grow larger and longer until they are finally obtained in needle shapes when the sulphuric acid excess is relatively large.

From a practical point of view, the club-shaped crystals filter well, but they are not so easy to wash and they contain a significant amount of unreacted phosphate rock. The relatively short lamellar crystals give better results from all points of view.

The needle-shaped crystals generally give good crystallization of the mother liquor, but losses in washing are greater than with those mentioned above.

3) Percentage of solids in suspension.

This factor has a very definite influence.

The thicker the slurry, the greater the growth of the crystals. Naturally, there is a practical limit to the thickening, as when there is too much of the solid phase present, the slurry becomes too stiff and the agitation in the reactor vessels is inadequate so that the reagents are not properly mixed.

In our factory we have obtained the best results with approximately 23-25% of solid phase.

4) Attack rate.

For a given volume of reactor vessels, the crystallization is better when the attack rate is lower. Thus there should be some advantage in carrying out the reaction in a large volume of reactor vessels, but here the limits are set by (a) the investment costs and the power consumption for the agitators and (b) by the fact that above a certain value the increase in the volume of reaction space brings practically no advantage.

For practical purposes, the plants now in use have a volume of 2 to 3 m³ per ton of P₂O₅ per day.

In our factory, where we use Gafsa phosphate, we have reactors to a total volume of 130m³ for a daily output of 70 tons P₂O₅.

5) Temperature.

The influence of the temperature is very similar to that of the excess of sulphuric acid.

The micrographs in Fig. 10, representing 3 trials carried out under identical conditions, apart from the temperature, show this clearly.

At 80° the crystals are lamellar, at 65° there is a mixture of shapes, while at 50° there is only the club-shape and they are larger in size.

But these results are valid only within the limits of the conditions which give crystallization of gypsum. As soon as a higher temperature or concentration gives rise to the formation of hemi-hydrate, other phenomena arise which alter these conclusions completely.

It should, moreover, be noted that in the temperature range (70 - 80°) within which we have to work for other reasons such as viscosity, foaming, cooling troubles, etc., the influence of temperature on crystallization is very slight.

6) Interfering ions.

This factor has a somewhat theoretical interest as there is little we can do about it.

Professor Forestier's work has shown that polyvalent ions favour lamellar crystallization of gypsum. This may explain why some rocks rich in Fe and Al are easy to work in phosphoric acid manufacture.

Summary of Results.

We can now repeat the table given at the end of the first part and complete by adding the variations in the quality of the crystallization.

Nature of Factor	Variation of Factor	Influence on P ₂ O ₅ content of crystal	Influence on quality of crystallization
P ₂ O ₅ conc. of acid	↗	↗	↘
H ₂ SO ₄ conc.	↗	↘	↗
% solid in suspension	↗	↘	↗
Attack rate	↗	↗	↘
Temperature	↗	↘	↗
Interfering ions	↗	↗	↗

A study of this table shows in a striking fashion how the effects of the different factors studied work together in one direction on the co-crystallized P₂O₅ and in the other on the quality of crystallization. Thus, any variation in one of the parameters tending to reduce the content of co-crystallized P₂O₅ improves the quality of crystallization.

One can thus say that with certain reservations (not working within the hemi-hydrate zone, for instance) the assessment of

the co-crystallized P_2O_5 constitutes a reliable criterion of the efficiency of a manufacturing technique.

We must note one exception to this rule - the influence of the interfering cations; however, in practice, these ions are present in the raw phosphates and we have no means of controlling their strength. We would observe that this is a chemical factor, while all the others are physical.

INTERPRETATION OF THE RESULTS.

Is there an explanation for the parallel actions of the different factors on the co-crystallization and the quality of the crystallization? We think there is, but before we put forward our hypothesis, we shall first examine what is known of the mechanism of the formation of gypsum crystals in a continuous reactor for the manufacture of phosphoric acid.

This mechanism occurs in two phases:

- a) appearance of SO_4^{--} and Ca^{++} ions
- b) precipitation (formation of seeds
(enlargement of crystals

Appearance of ions.

The formation of the SO_4^{--} ions is the simplest. The concentrated sulphuric acid is diluted and dissociates in the phosphoric acid. The SO_4^{--} ions appear at once.

The Ca^{++} ion cannot appear until the phosphate rock has been attacked by the H^+ ion, although this is also a fairly rapid reaction. Along with the Ca^{++} ions, it also liberates $H_2PO_4^-$ and HPO_4^{--} .

Precipitation.

As the liquor is saturated, the appearance of the Ca^{++} and SO_4^{--} causes a certain amount of supersaturation which constitutes our precipitation potential, responsible for the formation of seeds and the enlargement of crystals. The higher this potential, the greater the formation of seeds. The seeds as they multiply extend the active crystallization surface and reduce the average distance.

As regards the quality of crystallization, we wish to form the smallest possible number of seeds, since the size of the crystals is in inverse proportion to the number of seeds.

We therefore wish to reduce the precipitation potential to a minimum. In theory, this can be done. We should require to introduce slowly into a large amount of phosphoric acid appropriately seeded with calcium sulphate crystals and agitated to just the right degree, very diluted solutions of SO_4^{--} ions

and Ca^{++} ions (for instance, a solution of monocalcium phosphate thinly distributed through the phosphoric acid).

But, of course, in plant practice things are not at all like this. For one thing, we are always trying to reduce the size of the equipment which means that the reagents must be added faster. For another, the Ca^{++} source is the solid natural phosphate rock. When it is attacked by the phosphoric acid, a highly concentrated solution of Ca^{++} ions forms round each particle. When the SO_4^{--} ions arrive in this zone, the precipitation potential is high although the conditions averaged over the mass of the reaction medium may be those most favourable to crystallization.

But then - and this is where our hypothesis comes in, - in this zone where there is a high content of Ca^{++} and also HPO_4^{--} , we have the components of dicalcium phosphate. In the pure phosphoric acid medium precipitation is not possible, but in the presence of SO_4^{--} simultaneously with the precipitation of the calcium sulphate, there could be some HPO_4^{--} ions incorporated into the crystal lattice. This is a possibility, as we have shown, because of the similarity of the crystalline properties of calcium sulphate and dicalcium phosphate dihydrate.

We suggest that it is in these microscopic zones with a high Ca^{++} concentration that there would occur formation of the crystal seeds containing co-crystallized P_2O_5 , while the enlargement of the existing crystals would occur in the more homogeneous zones.

This hypothesis would account for the parallel in the influence of the various factors studied on the crystal size and co-crystallization. Any influence tending to increase the Ca^{++} concentration and hence the crystallization potential around the phosphate particle, would reduce the crystal size and increase co-crystallization. Conversely, any influence tending to reduce this concentration or favouring the diffusion of the Ca^{++} ions would have the opposite effect.

Thus:

- 1) a higher P_2O_5 concentration in the acid increases the attack rate and has a harmful influence
- 2) a higher H_2SO_4 concentration brings more SO_4^{--} ions to the phosphate and reduces the Ca^{++} concentration. Thus, it has a beneficial influence.
- 3) an increase of the percentage of solids in solution rapidly reduces the supersaturation and aids the diffusion of the Ca^{++} ions. Thus, it has a beneficial influence.
- 4) an increase in the attack rate increases the supersaturation. Thus, it has a harmful influence.
- 5) an increase in the temperature will have two opposed effects:
(a) it will increase the attack of the phosphate (harmful

influence) and (b) it will aid the diffusion of the reagents (beneficial influence). The latter seems preponderant, but we have shown that, in any case, the temperature does not have much influence.

Throughout this paper we have not mentioned the quality of the agitation in the reaction vessels, because its variations are difficult to distinguish precisely. But in the light of the foregoing, it is obvious - and industrial experience will confirm this - that it has very great influence.

APPENDIX I.

References

WAGGAMAN - Phosphoric acid, phosphates & phosphatic fertilizers
P. 185

The author notes that this form of P_2O_5 is citrate-soluble and assumes that the HPO_4^{--} ion is substituted for the SO_4^{--} ion, but he does not offer any proofs.

He also notes the influence of the sulphuric acid and phosphoric acid concentration of the medium.

An excess of sulphuric acid reduces the concentration of P_2O_5 in the gypsum while a higher concentration of P_2O_5 in the phosphoric acid increases it.

HILL HENDRICKS - Ind. Eng. Chem. (1935)

These authors studied the influence of temperature on the P_2O_5 content of the gypsum by crystallizing out the gypsum by the evaporation of solution of phosphoric acid saturated with calcium sulphate at different temperatures.

They found that the content falls as the temperature rises. Even the hemi-hydrate contains some P_2O_5 .

Their chemical analysis gives a ratio $\frac{P_2O_5}{CaO} = \frac{1}{2}$ which is

the composition of dicalcium phosphate.

The X-ray spectra of the P_2O_5 containing gypsum and of pure calcium sulphate cannot be distinguished from each other, whereas the characteristic dicalcium phosphate lines can be clearly seen when a mixture of equivalent amounts of gypsum and dicalcium phosphate is examined. The authors conclude that there is a single phase which can still be observed even after heating to 200 and 400°.

CAMPBELL COUTTS - March 1947.

These authors assert that the X-ray spectra of gypsum and dicalcium phosphate are too much alike for definite conclusions to be reached.

Furthermore, they dare not rely on the results of analysis because their gypsum samples did not contain more than 1% P_2O_5 which, with due allowance for analytical errors, made a quantitative appreciation of one component against the other rather unreliable.

They could offer no solution to this problem.

H. FORESTIER & G. KREMER

Extract from C.R. Acad. Sci. 25/2/52.

Influence of interfering ions in solution on the crystalline face of the precipitated gypsum.

APPENDIX II.

Conversion of the curves of Figure 6. into those of Figure 7.

Let Y be the factor which governs the P_2O_5 in the instantly formed gypsum as a function of the percentage of crystal in suspension; the curves of Fig. 6. will then represent the factor:

(1) $\frac{1}{G} \int Y dG$ with $G = \% \text{ gypsum of volume in suspension.}$

To find the factor Y, we plotted the experimental factors on a logarithmic graph, and showed that they corresponded to the following:

For PO4H3	at 340	grs/l	P2O5	:	% P2O5 of gypsum = 1,70	G ^{-1/4}
For "	at 200	" "	"	:	" " = 1,48	G ^{-1/3}
For "	at 100	" "	"	:	" " = 1,29	G ^{-1/2,5}

either as the formula: $\frac{1}{K G} \frac{1}{n}$ or $\frac{K}{\sqrt[n]{G}}$

we may by equalizing with (1) above express it as:

$$K G^{-\frac{1}{n}} = \frac{1}{G} \int Y dG$$

by extracting Y

$$\int Y dG = K G^{\frac{n-1}{n}}$$

the factor Y is therefore derived from:

$$K G^{\frac{n-1}{n}}$$

or:

$$Y = \frac{n-1}{n} K G^{-\frac{1}{n}}$$

APPENDIX III.

Analysis of co-crystallized P_2O_5 .

Preparation of sample.

The sample of gypsum is washed three times by decantation with distilled water, then three times with alcohol and finally with ether on a Buchner filter. It is then stove-dried for 5 minutes at 70° . The gypsum obtained in this way is dry and not dehydrated.

Dissolving.

The choice of solvent is important because the gypsum must be dissolved without solubilizing the unreacted phosphate. The gypsum can be dissolved in a sufficient amount of distilled water containing a few drops of hydrochloric acid (pH 3-4) to prevent the possible precipitation of phosphate and calcium. This solution will contain only the co-crystallized P_2O_5 and its dilution makes it suitable for colorimetric determinations. If it is evaporated by boiling in the presence of a slight excess of sulphuric acid which will prevent the P_2O_5 from passing back into the gypsum, the determination may be carried out by the molybdic method. The ammonium citrate dissolves about 10gr/l. Using this solution, the P_2O_5 can be precipitated in the form of ammonium magnesium phosphate. However, since we are generally handling very weak solutions, it is usual to add a known amount of P_2O_5 and to make a previous determination of the weight of magnesium pyrophosphate formed from this. Then the extra precipitate obtained will correspond to the P_2O_5 contained in the gypsum.

This method avoids the error which might be caused by the solubility of the pyrophosphate in the citrate and the precipitation is made more complete by entrainment. The method is then exact enough for industrial analyses.

Reagents: Ammonium citrate

Dissolve 400 g of citric acid in ammonia with density 0.9 and make up with this to 1 litre;

Magnesium reagent

150 g of $Mg_6Cl_2 \cdot H_2O$, and 150 g of NH_4Cl per litre

Ammonia

Density : 0.92

Dilute phosphoric acid

Weigh about 10 g of 85% (60 Bé) phosphoric acid and make up to 1,000 ml.

APPENDIX III. (Continued)

Pure gypsum (Prolabo)

Washing Solution

200 ml NH_4OH and 5 g NH_4Cl added per litre

Precipitation in the presence of synthetic gypsum (control)

Weigh 2.5 g of pure gypsum and add to 100 ml ammonium citrate. When completely dissolved, add about 50 ml of water to aid quantitative filtration of the solution. Wash the filter and dilute with water so as to obtain a total volume of about 250 ml. Then add successively:

- 60 ml NH_4OH
- 25 ml H_3PO_4 (precision pipette)
- 10 ml magnesium mixture

stir with a glass rod.

Leave overnight to stand. After filtering, washing and calcining, weigh the $\text{Mg}_2\text{P}_2\text{O}_7$. This is the weight of P to be subtracted from the precipitations with the gypsum containing P_2O_5 .

Determination of co-crystallized P_2O_5 .

The procedure is identical, except that gypsum from the plant is used.

From the final weight P' , the calculation is:

$$\% \text{P}_2\text{O}_5 \text{ in gypsum} = (P' - P) 0.0255$$

FIGURE No. 1

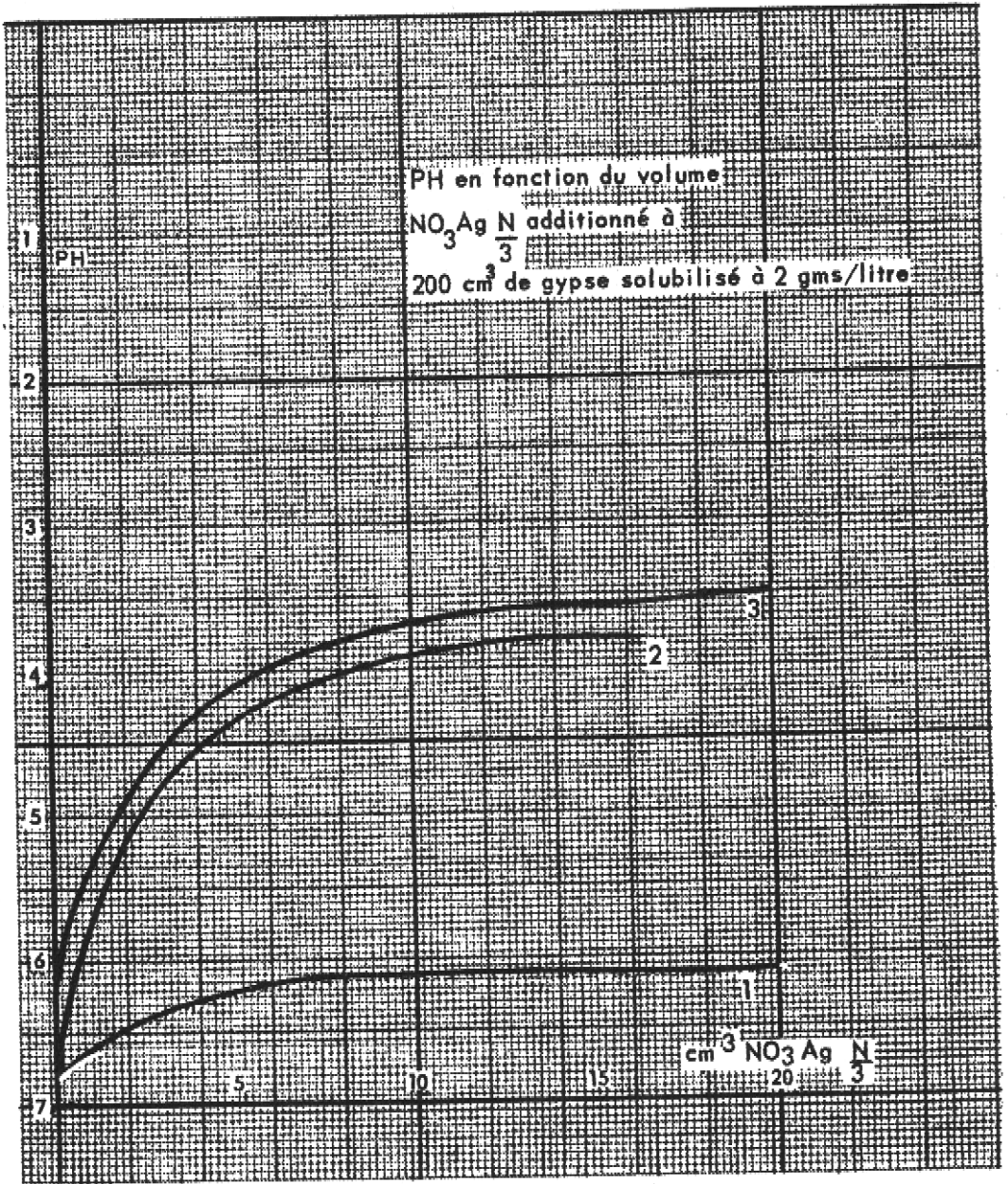


FIGURE no 1

Variation du PH en fonction du volume
 de nitrate d'argent $\frac{\text{N}}{3}$ ajouté.

Courbe 1 : gypse pur

Courbe 2 : gypse à 3,6 % P205 fabriqué avec des produits purs

Courbe 3 : gypse à 5,4 % P205

Variation of the PH in proportion to the volume
 of silver nitrate $\text{N}/3$ added.

Curve 1 : pure gypsum

Curve 2 : gypsum with 3.6% P205 produced from pure products

Curve 3 : gypsum with 5/4% P205

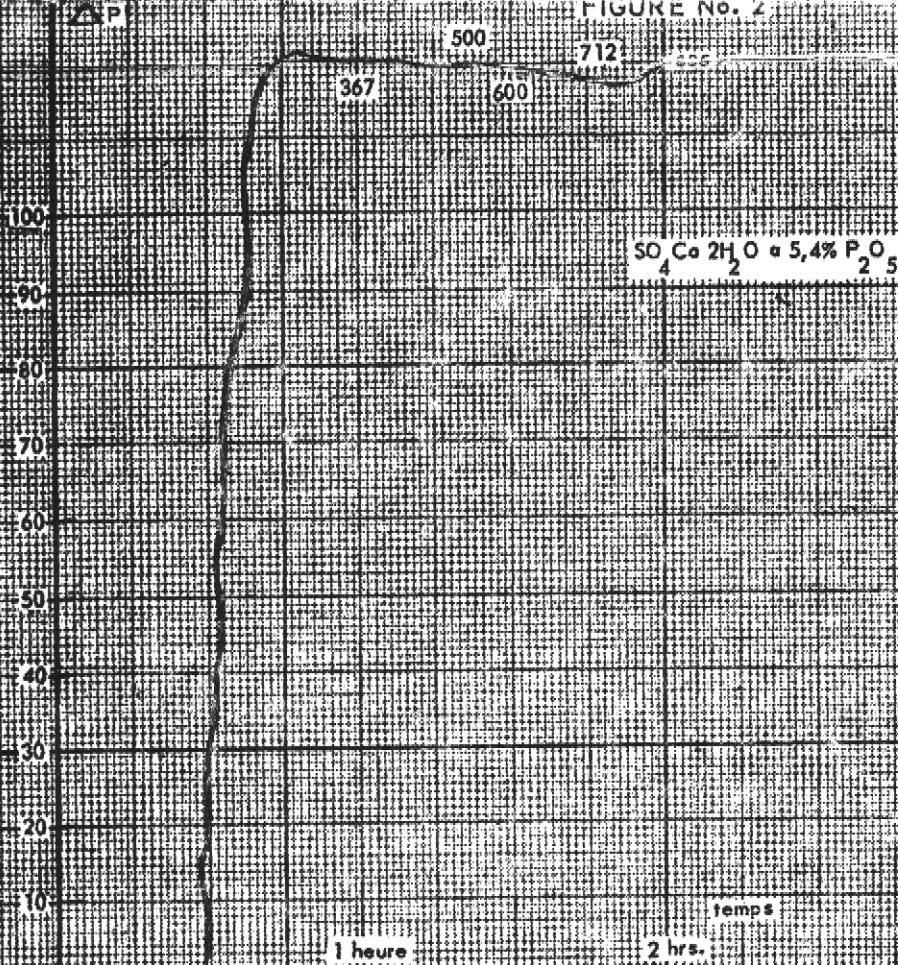


Fig 2

Thermobalance

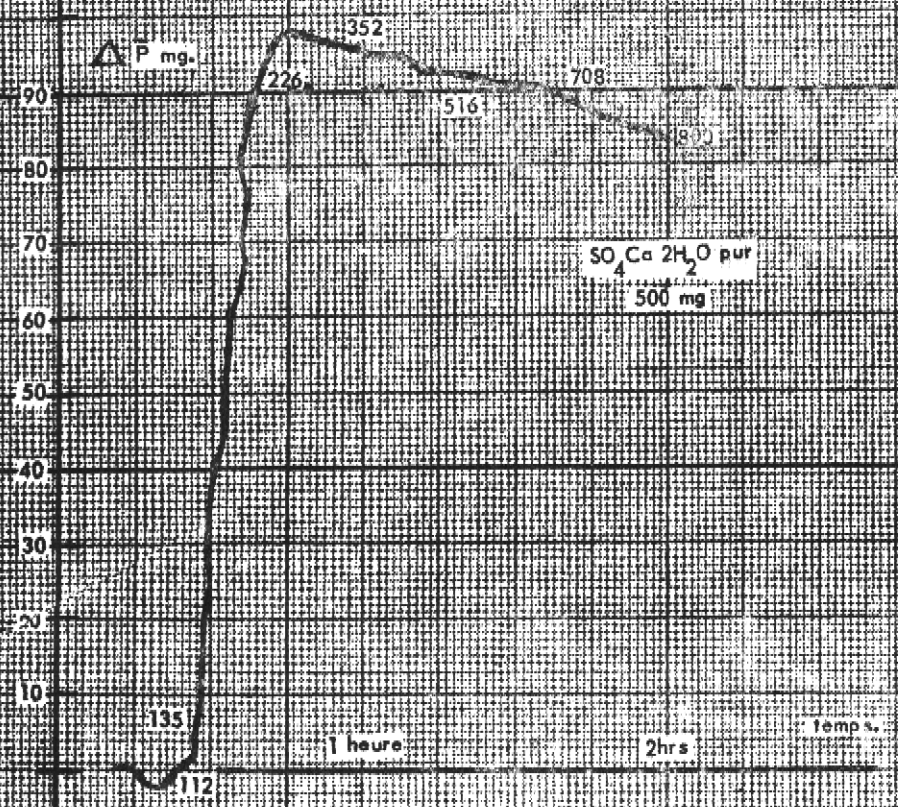


FIGURE No. 3

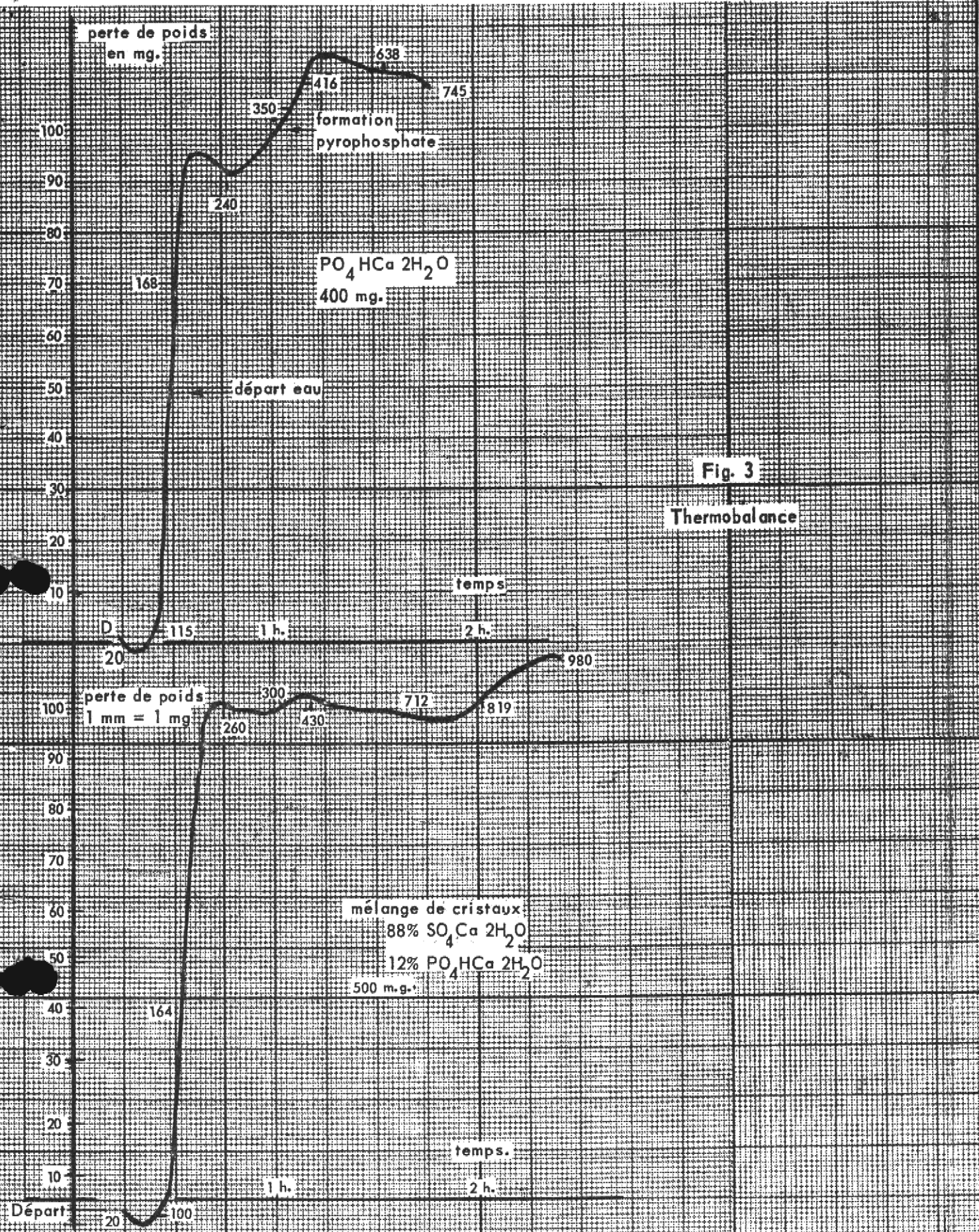


Fig. 3

Thermobalance

FIGURE No. 4

Analyses Thermodifferencielles

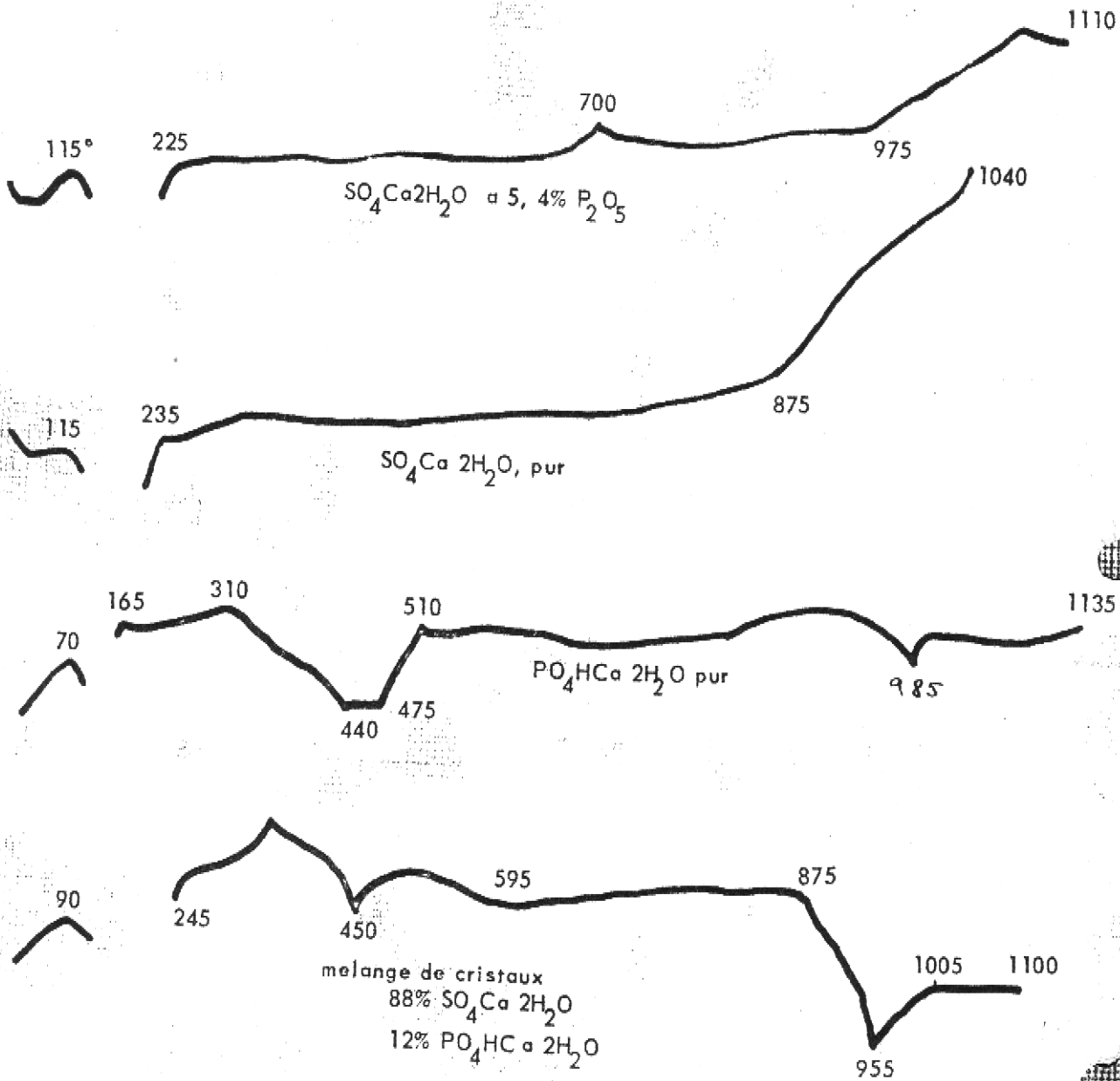


FIGURE No. 5

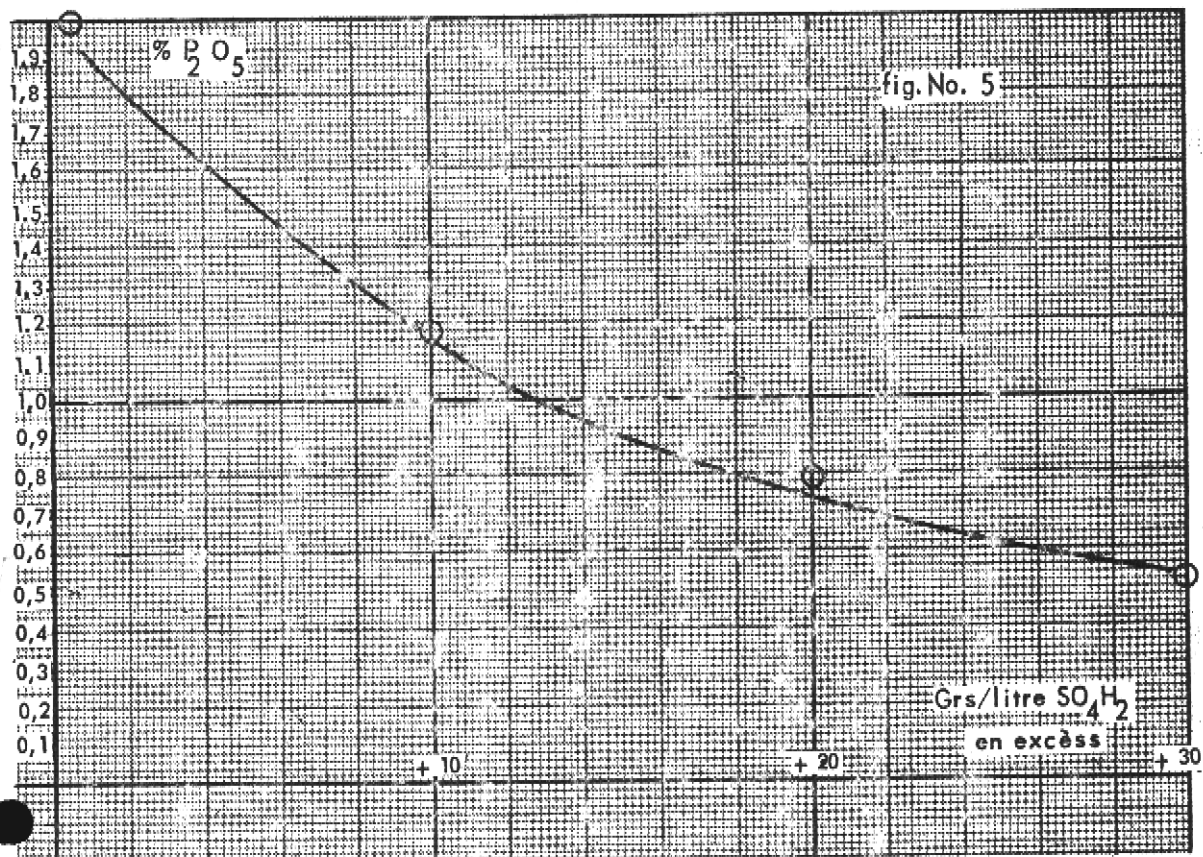


FIGURE no 5

Pourcentage de P205 dans le gypse en fonction de k'excès d'acide sulfurique présent dans le milieu phosphorique précipitant.

(Excès exprimé en grs/litre)

Percentage of P205 in the gypsum in proportion to the surplus sulphuric acid present in the surrounding phosphoric precipitant.

FIGURE No. 6

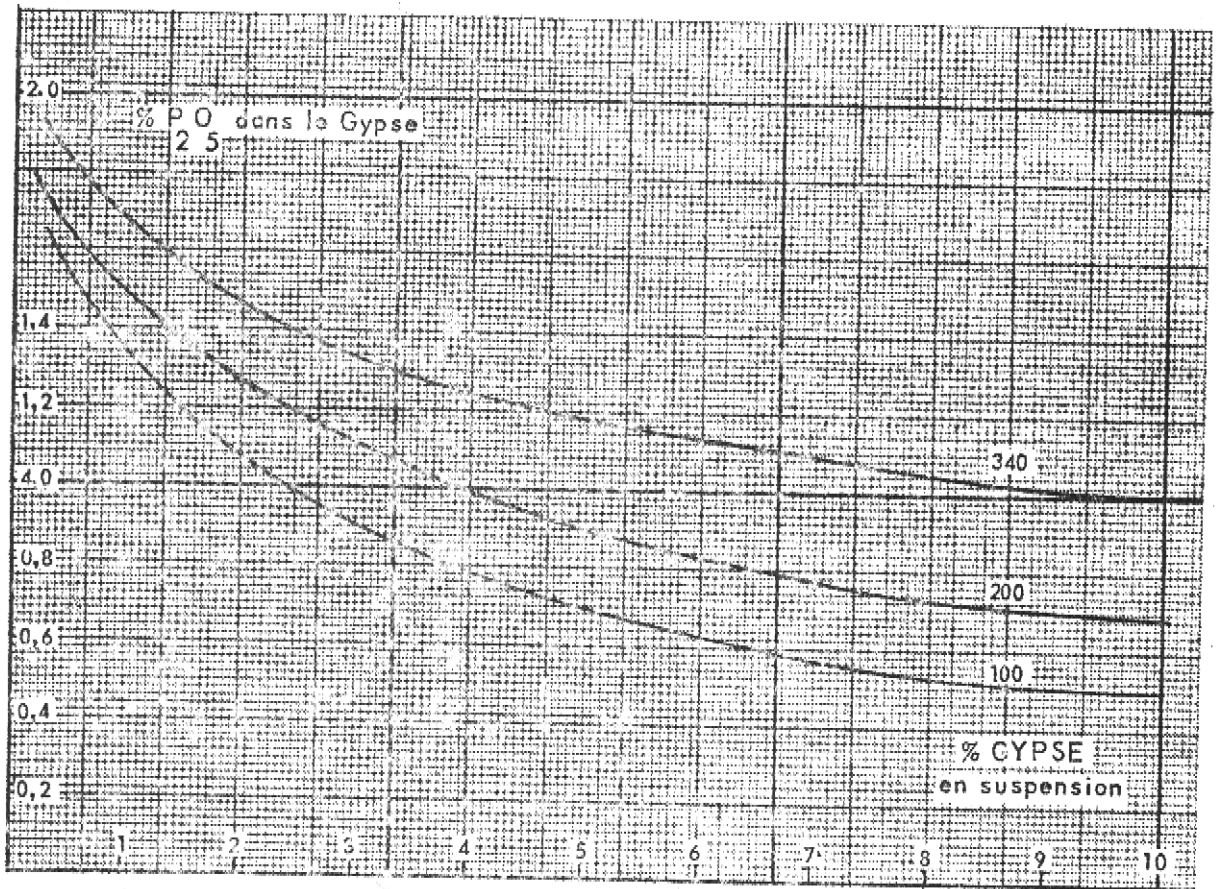


FIGURE no. 6

P₂O₅ dans le gypse en fonction du pourcentage de solide en suspension et de la concentration de l'acide phosphorique (teneurs des échantillons moyens)

P₂O₅ in the gypsum in proportion to the percentage of solid in suspension and the concentration of the phosphoric acid (strengths of average samples)

FIGURE No. 7

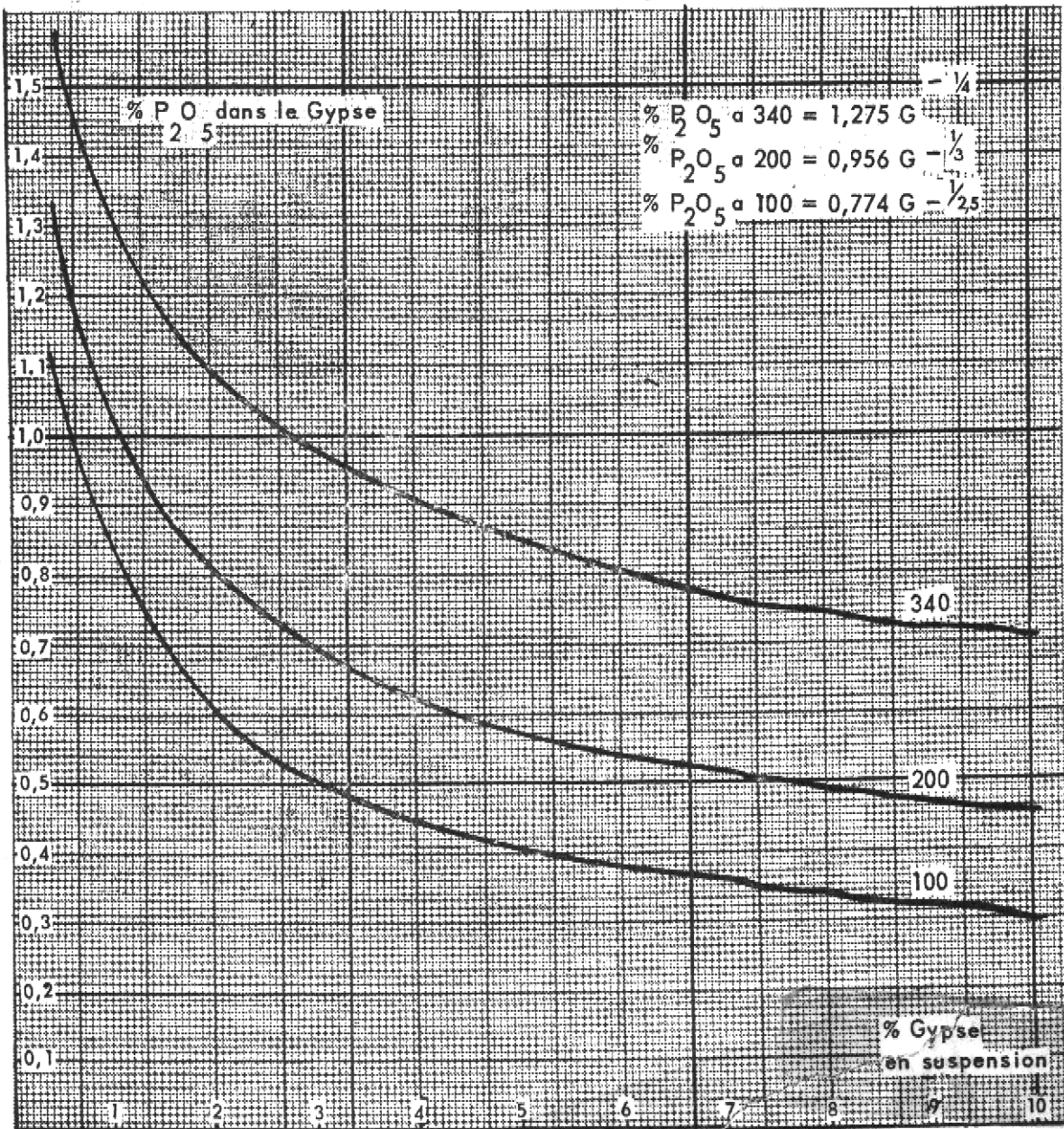


FIGURE no. 7

P205 dans le gypse en fonction du pourcentage de solide en suspension et de la concentration de l'acide phosphorique (teneur instantanée)

P205 in the gypsum in proportion to the percentage of solid in suspension and the concentration of the phosphoric acid (momentary strength)

FIGURE No. 8

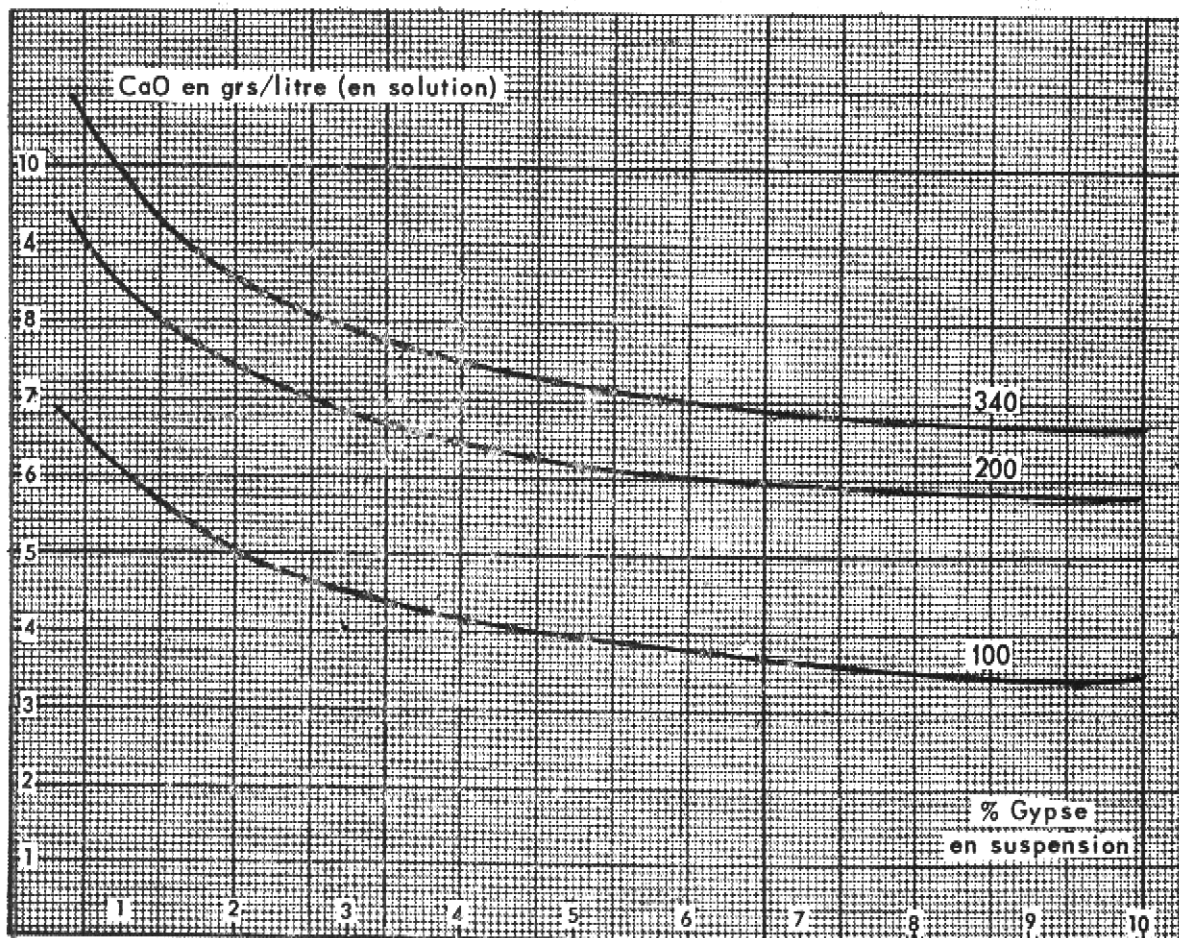


FIGURE no. 8

Concentration de l'ion Ca^{++}
(exprimé en grs/l CaO) en fonction
du pourcentage de solide en suspension

Concentration of Ca^{++} ion
(expressed in grs/litre CaO)
in proportion to the percentage
of solid in suspension

FIGURE No. 9

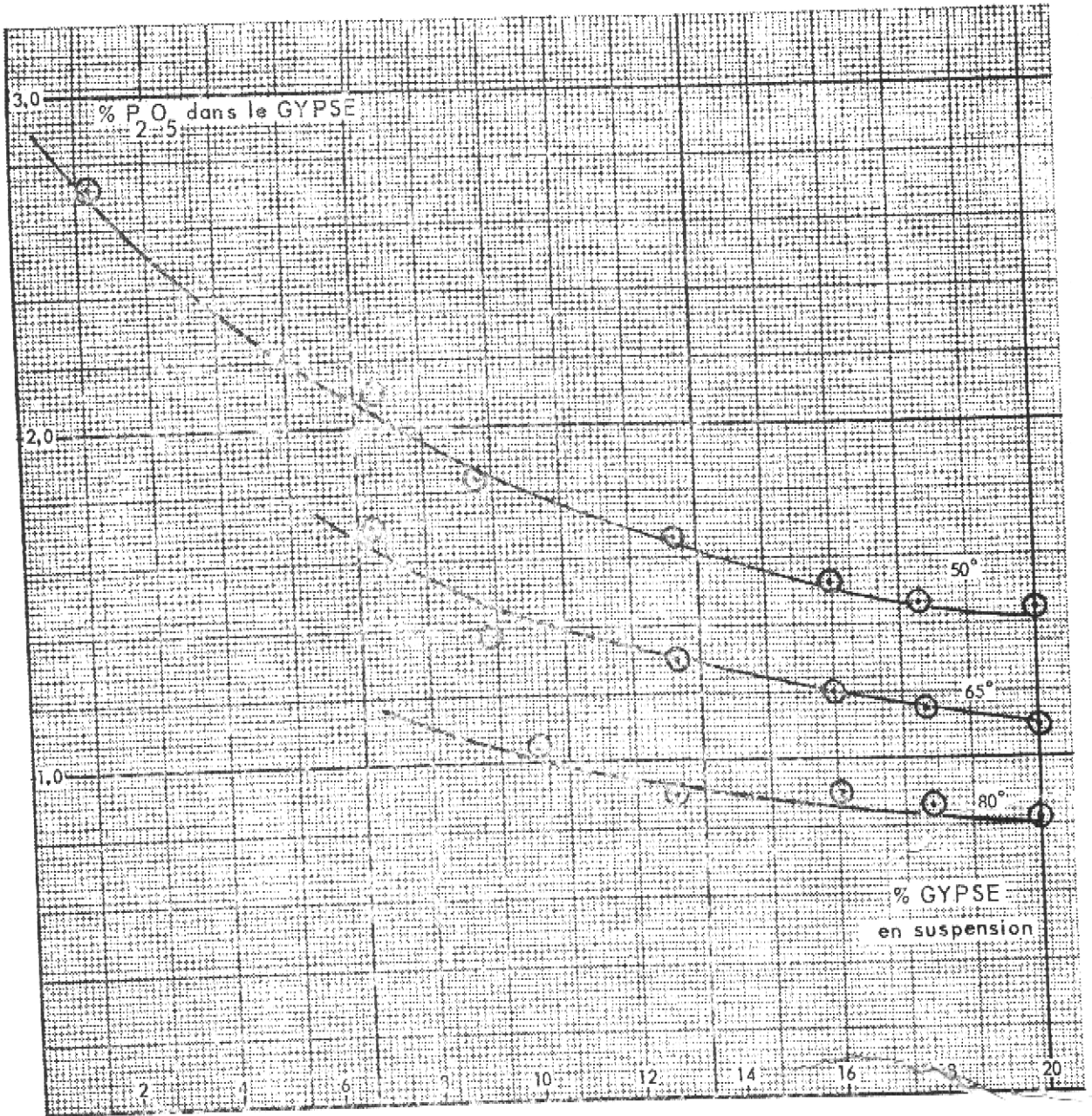


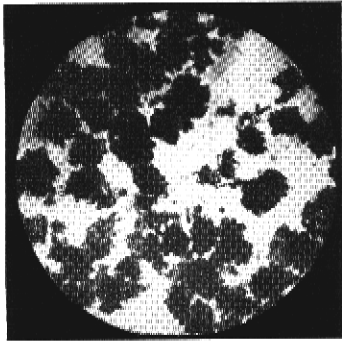
FIGURE no. 9

Influence de la température et
du pourcentage de solide en
suspension sur le P_2O_5 dans le gypse

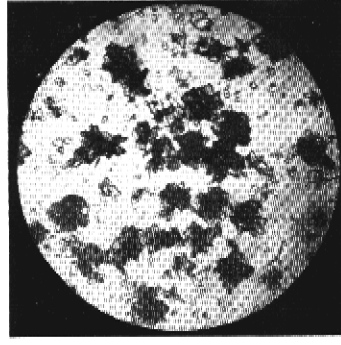
(échantillons moyens)

Influence of the temperature and
the percentage of solid in suspension
on the P_2O_5 in the gypsum

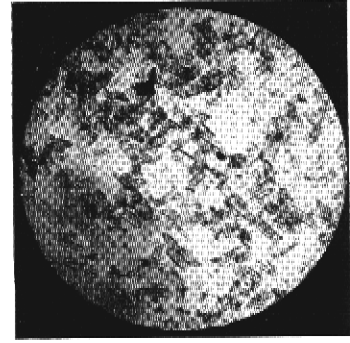
(average samples)



50°



65°



80°

Figure 10

Influence de la température
sur la forme cristalline.

Influence of temperature
on crystalline form.