

ISMA* Technical Conference

**Wiesbaden, Germany
11-15 September 1961**

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*



SUPERPHOSPHATE

MANUFACTURERS' ASSOCIATION

TECHNICAL COMMITTEE · COMITE DES TECHNICIENS

CONFIDENTIAL

LE/61/53

Received: 2nd June 1961.

TECHNICAL MEETINGS - WIESBADEN

This paper will be presented at the Technical Meetings in Wiesbaden from September 11th to 15th, 1961. It must not be published prior to that date, and, in any case, it must not be published without the permission of the author.

PRODUCTION OF CONCENTRATED PHOSPHORIC ACID FROM PHOSPHATES WITH HIGH IRON AND ALUMINIUM CONTENT. BEHAVIOUR AND PRECIPITATION OF THESE ELEMENTS. MEANS FOR CONTROLLING THEM IN ORDER TO PRODUCE AN ACID FREE OF MATTER IN SUSPENSION.

By A. Michot,
Société Métallurgique de Prayon,
Belgium.

I. INTRODUCTION

The acids obtained by the wet process give rise to the formation of solid deposits in various quantities and of different compositions, according to a very large number of factors. A freshly prepared phosphoric acid from which a first deposit has been separated continues forming precipitates. This phenomenon may continue perceptibly for a considerable time (several weeks or several months). Solid matter is formed even in weak phosphoric acids.

Generally speaking, the higher the P2O5 concentration of the acid the stronger the precipitation. This results in increased troubles in the manufacturing process (congestion of piping, the necessity of frequent cleaning of the tanks, the complications which may arise during subsequent utilisation of the acid, etc...).

Moreover, in certain cases, important P2O5 losses in the deposits are sustained. It is obvious that these harmful effects should be remedied to the greatest possible extent.

Let us consider successively three types of phosphoric acid obtained from phosphates with increasing Fe2O3 and Al2O3 contents:

	Contents in %	
	Fe2O3	Al2O3
Phosphate A	0.47	0.40
Phosphate B	1.30	0.92
Phosphate C	2.20	1.10

The preparation of phosphoric acid by sulphuric acid attack and filtration of the slurry obtained does not present any problems particularly related to the Fe₂O₃ and Al₂O₃ contents of these phosphates.

We shall not therefore describe this operation, but merely indicate the analyses of the weak phosphoric acids which we used for preparing other, more concentrated acids with which our investigations were particularly concerned.

	Contents in %		
	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃
Phosphoric Acid A	28.7	0.29	0.38
Phosphoric Acid B	29.1	0.84	0.54
Phosphoric Acid C	30.6	2.25	1.10

Precipitations appear in the course of concentration; they become all the more important as one passes from type A acids to those of type C. These phenomena are the subject of our survey.

This includes physical measures concerning apparent volumes and weights of deposits. Centrifugations lasted thirty minutes in a gravitational field of about 1.500 g. Filtrations were effected on polyvinyl chloride cloths and the deposits obtained were washed with alcohol and dried before analysis.

In order to reveal the presence of certain well-defined compounds in the deposits, we have proceeded as follows:

Having found by chemical analysis the concentrations of the main anionic and cationic components, we derived from this the H⁺ ion content by calculating the difference between the sum of the anions and that of the cations expressed in milli-equivalents in 100 grams (meq/100 g).

In the deposits in which one salt was definitely predominant in relation to the others, we were led to calculate its existence according to the results of chemical analyses. As we generally knew its crystalline characteristics, it was enough to examine by the microscope a sample of the undried deposit in order to check our forecasts.

This procedure, which cannot be applied in all cases, enabled us to reveal with certainty the presence of calcium sulphate and fluoride, and two types of ferric acid phosphates: FeH₃(PO₄)₂·2.5 H₂O and Fe(H₂PO₄)₃·2H₂O.

Certain analytical results obtained with deposits in which the aluminium content is not negligible as compared with that of iron indicate that aluminium would also precipitate in the form of aluminium phosphates. (Reference 1).

The indication of sodium and potassium fluosilicates is more difficult. Among the deposits examined, we found none of which the major part was made up of one of these salts. However, in the deposits collected from type A phosphoric acid concentrators in the works, we found in some cases sodium fluosilicate contents up to 65%.

In certain favourable cases, fluosilicates can be identified by the following reaction:



In the course of interpretation of numerous analytical results, we have been led to admitting the existence of sodium and potassium acid fluorides (References 2 and 3). However, microscopic examination of the deposits never showed us indisputably the rhombohedral shape of NaF.HF, nor the cubic one of KF. x HF, which may be accounted for by the fact that these substances attack the glass plate of the microscope and that the geometric shape of the crystals alters; the smaller the crystals, the quicker this alteration occurs. The chemical analysis of the aqueous extract of certain deposits indicates the putting in solution of hydrofluoric acid, which fits in well with the hypothesis of the presence of acid fluorides.

These latter points, which depart from our subject proper, have not been studied in detail.

A few photos of various salts, definitely identified due to their very high concentration are shown at the end of this report (photos I to V).

II. PHENOMENON OF PRECIPITATION IN PHOSPHORIC ACIDS PREPARED FROM TYPE A PHOSPHORIC ACID

1) Physical Measurements

Treatment of acid		Centrifugations and decantations interrupted by rest periods	Filtrations interrupted by rest periods
Starting hours of centrifugations(x)		2 - 24 - 46 - 68 - 100	
Starting hours of filtrations(x)			24 - 72 - 168 - 264 - 336 for 28.7% P2O5 acid and 1 - 24 - 384 for 46.3% P2O5 acid
Phosphoric acid % P2O5	Density	Total apparent volume of slurry collected (milli-litre/litre of acid)	% by weight of total deposit with respect to the phosphoric acid
28.7	1.306	35	0.76
46.3	1.555	95	2.10

(x) Times, in hours, are reckoned from the end of the phosphoric acid production reaction.

2) Chemical analysis of the deposits

A) Main anionic and cationic components of the deposits collected by successive filtrations and rest times of the acids.

Phosphoric acid at start (% P2O5)	28.7	46.3
Density	1.306	1.555
Total time in hours	336	384
Anionic components	Total quantity (grams) of substance eliminated by 4 litres of phosphoric acid	
PO_4^{3-}	1.16	23.95
SO_4^{2-}	13.83	45.98
SiF_6^{2-}	7.59	12.94
F^-	5.69	14.56
Cationic components		
Ca^{++}	5.56	18.75
Na^+	4.22	12.28
K^+	1.82	2.01
Fe^{+++}	0.06	0.26
Al^{+++}	0.07	0.37
H^+	0.21	1.07

B) Nature of the main salts to be found in the deposits.

a) Presence of calcium sulphate.

Phosphoric acid A - concentration 28.7% P2O5 -
deposit collected between 72 and 168 hours (4.9 gr/4
litres of acid) - (photo No. 1).

Anions	%	Meq/100 gr.	Cations	%	meq/100 gr.
PO4 ⁼⁼	4.28	135	Ca ⁺⁺	25.7	1,285
So4 ⁼⁼	60.00	1,250	Na ⁺	2.65	115
SiF6 ⁼⁼	3.06	43	K ⁺	0.61	16
F ⁻	3.47	183	Fe ⁺⁺⁺	0.20	11
			Al ⁺⁺⁺	0.41	46
			H ⁺ (diff.)	0.138	138
Totals	70.81	1,611		29.71	1,611

Calcium sulphate reaches an approximate concentration of 86%.

b) Presence of sodium and potassium acid fluorides and fluosilicates.

Phosphoric Acid A - concentration 28.7% P2O5 -
deposit collected between 0 and 24 hrs (21.9 gr/4 litres
of acid).

Anions	%	meq/100 gr.	Cations	%	meq/100 gr.
PO4 ⁼⁼	1.60	51	Ca ⁺⁺	7.4	370
So4 ⁼⁼	20.9	435	Na ⁺	15.0	650
SiF6 ⁼⁼	27.7	390	K ⁺	6.48	166
F ⁻	20.7	1,090	Fe ⁺⁺⁺	0.23	12
			Al ⁺⁺⁺	0.18	20
			H ⁺ (diff.)	0.748	748
Totals	70.9	1,966		30.04	1,966

The interpretation of the analytical results leads us to consider out of a total of 1,966 meq/100 gr.

390 meq in the form of (Na, K)₂ SiF6
426 meq of Na⁺, K⁺)
664 meq of H⁺) in the form of (NaK)F. x H F
1,090 meq of F⁻)

c) Presence of acid ferric phosphates.

Various ferric phosphates which are stable at a temperature of 25°C in certain P2O5 concentration areas are known (reference No. 4 and 5).

Phosphoric acid %P2O5 (approximate)	Nature of stable compound	Shape of the crystal
0.35 to 24	Fe PO4 . 2.5 H2O	amorphous
25 to 47	Fe H3(PO4)2 . 2.5 H2O	prismatic needles with 4 faces ending in two pyramids.
48 to 58	Fe (H2 PO4)3 . 2 H2O	small hexagonal plates.
58 and more	Fe (H2 PO4)3	long stretched small hexagonal plates.

Phosphoric acid A - concentration : 46.3% P2O5 - deposit collected between 1 and 24 hours : probably two crystals of the type (Fe, Al) (H2 PO4)3 2H2O are to be seen on photo No. 2.

C) Interpretation of the analytical results.

Phosphoric acid at start - %P2O5	28.7	46.3
Density	1.306	1.555
Total time in hours	336	384
Nature of the salts	milliequivalents precipitated in 4 litres of phosphoric acid	
CaSO4	278	937
(Na, K)2 SiF6	107	182
(Na, K)F. x HF		
{ Na ⁺ , K ⁺	124	403
{ H ⁺	176	362
{ F ⁻	300	765
(Fe, Al) H3 (PO4)2		
{ Fe ⁺⁺⁺ , Al ⁺⁺⁺	11	
{ H ⁺	11	
{ PO4 [≡]	22	
(Fe, Al) (H2 PO4)3		
{ Fe ⁺⁺⁺ , Al ⁺⁺⁺		55
{ H ⁺		110
{ PO4 [≡]		165
H3 PO4	15	590

b) Treatment of the acid.

Centrifugations followed by decantations and rest times, made several times with various phosphoric acids, enabled us to collect the following apparent volumes of deposits in suspension (ml/l) which we recorded as a function of time (hours) - (graphs 2 and 3).

Phosphoric acid % P2O5	Hours of starting of centrifugation																					
	1	2	21	24	25	46	47	48	69	70	72	92	94	96	120	128	168	176	192	202	206	
	Total apparent volumes of the deposits (ml/l)																					
29.1		10		37.5		45									55							
38.9	20				50		60		65													
48.7	30			40				50			70			90	105		125		135		145	
54.6		90	105							125			145			170		210		220		

B) Weights of dry deposits.

Treatment of the acid.

Phosphoric acids of various concentrations were left at rest without stirring and then filtered; afterwards the cycle of operations was started all over again. The various deposits collected were washed with alcohol, dried and weighed (graphs 4 and 5).

Phosphoric Acid at start % P2O5	Density	Hours of beginning of filtration	% of dry slurry with respect to the weight of phosphoric acid at start	Total of dry slurry with respect to the weight of phosphoric acid at start
29.1	1.338	93	0.31	0.31
		120	0.20	0.51
		552	0.25	0.76
38.9	1.470	24	0.66	0.66
		336	0.10	0.76
50.5	1.640	48	2.03	2.03
		70	0.36	2.39
		120	0.19	2.58
		168	0.18	2.76
		288	0.10	2.86
54.6	1.705	24	4.10	4.10
		72	0.67	4.77
		240	0.04	4.81

2) Chemical analysis

A) Main anionic and cationic components of the deposits collected by successive filtrations and rest periods of the acids.

Phosphoric acid at start % P2O5	29.1	38.9	50.5	54.6
Density	1.338	1.470	1.640	1.705
Total time in hours	552	336	288	240
Anionic components	Total quantity (grams) of substance eliminated for 4 litres of phosphoric acid.			
PO ₄ ^{III}	0.58	1.34	82.94	162.23
SO ₄ ^{II}	5.39	19.32	7.09	61.86
SiF ₆ ^{II}	5.15	8.57	20.12	20.55
F ⁻	11.19	1.73	0.00	0.08
SiO ₃ ^{II} (x)	-	-	13.00	10.90
Cationic components				
Ca ⁺⁺	8.38	8.40	13.05	29.62
Na ⁺	2.18	3.20	11.75	10.15
K ⁺	1.22	1.19	5.78	6.89
Fe ⁺⁺⁺	0.00	0.02	10.84	15.35
Al ⁺⁺⁺	1.05	0.13	0.66	4.29

(x) The presence of this excess of silicate is due to attack of our concentration equipment.

E) Nature of the main salts found in the deposits.

a) Presence of calcium fluoride.

Phosphoric acid B. concentration 29.1 % P2O5 - deposit collected between 0 and 48 hours (10.6 gr/4 litres).

F⁻ content = 1,620 meq/100 gr = 30.8 %

Ca⁺⁺ content = 1,745 meq/100 gr = 34.9 %

Phosphoric acid B. concentration 29.1 % P2O5 - deposit collected between 0 and 93 hours (16.8 gr/4 litres) (photo 3).

Anions	%	meq/100 gr	Cations	%	meq/100 gr
PO ₄ [≡]	1.07	34	Ca ⁺⁺	11.07	553
SO ₄ ⁻	15.7	327	Na ⁺	11.2	487
SiF ₆ ⁻	24.0	338	K ⁺	6.43	165
F ⁻	23.0	1,210	F ⁺⁺⁺	0.00	0
			Al ⁺⁺⁺	0.01	1
			H ⁺	0.703	703

Interpretation of analytical results

Ca F ₂		<u>meq/100 gr</u>	226
(Na,K) ₂ SiF ₆			338
Ca SO ₄			327
(Na,K)F. x HF	Na,K		314
	H		670
	F		984
H ₃ PO ₄			34

b) Presence of calcium sulphate.

Phosphoric acid B. concentration 38.9 % P2O5 - deposit collected between 24 and 336 hours (5.8 gr/4 litres).

Anions	%	meq/100 gr	Cations	%	meq/100 gr
PO ₄ ^{III}	3.79	120	Ca ⁺⁺	22.4	1,120
SO ₄ ^{II}	51.5	1,070	Na ⁺	1.72	75
SiF ₆ ^{II}	6.03	85	K ⁺	2.93	75
F ⁻	3.10	164	Fe ⁺⁺⁺	0.00	0
			Al ⁺⁺⁺	0.34	38
			H ⁺	0.131	131

Calcium sulphate reaches an approximate concentration of 74%. Phosphoric acid B. concentration 50.5 % P2O5 - deposit collected between 0 and 20 hours (98.5 gr/4 litres). (photo 4).

c) Presence of acid iron and aluminium phosphates of type (Fe,Al) (H₂PO₄)₃

Phosphoric acid B. concentration 50.5 % P2O5 - deposit collected between 48 and 72 hours (28,5 gr/4 litres).

Anions	%	meq/100 gr	Cations	%	meq/100 gr
PO ₄ ^{III}	67.1	2,120	Ca ⁺⁺⁺	5.41	225
SO ₄ ^{II}	10.4	216	Na ⁺	0.77	34
SiF ₆ ^{II}	0.64	9	K ⁺	2.59	67
SiO ₃	1.87	49	Fe ⁺⁺⁺	11.0	590
			Al ⁺⁺⁺	0.51	57
			H ⁺⁺	1.421	1,421

Interpretation of the analytical results.

	<u>meq/100 gr.</u>		
	<u>Experimental</u>	<u>Theoretical</u>	<u>Difference</u>
Fe ⁺⁺⁺ , Al ⁺⁺⁺	647	647	
H ⁺	1,421	1,294	127
PO4 ⁼	2,120	1,941	179

Phosphoric acid B. concentration 50.5 % P2O5 - deposit collected between 168 and 288 hours (6.29 gr/4 litres) - (photo 5).

Anions	%	meq/100 gr	Cations	%	meq/100 gr
PO4 ⁼	64.7	2,040	Ca ⁺⁺	3.5	175
SO4 ⁼	8.9	185	Na ⁺	0.48	21
SiF6 ⁼	0.64	9	K ⁺	2.38	61
SiO3	4.29	113	Fe ⁺⁺⁺	10.6	570
			Al ⁺⁺⁺	0.32	36
			H ⁺	1,484	1,484

Interpretation of the analytical results.

	<u>Meq/100 gr</u>		
	<u>Experimental</u>	<u>Theoretical</u>	<u>Difference</u>
Fe ⁺⁺⁺ , Al ⁺⁺⁺	606	606	
H ⁺	1,484	1,212	272
PO4 ⁼	2,040	1,818	222

Phosphoric acid B. concentration 54.6 % P2O5 - deposit collected between 26 and 72 hours (45.5 gr/4 litres).

Anions	%	Meq/100 gr	Cations	%	Meq/100 gr
PO4 [■]	70.0	2,200	Ca ⁺⁺	1.14	57
SO4 [■]	2.04	42	Na ⁺	0.79	34
SiF6 [■]	1.19	17	K ⁺	2.59	66
			Fe ⁺⁺⁺	11.5	620
			Al ⁺⁺⁺	0.99	110
			H ⁺	1.372	1,372

Interpretation of analytical results.

	<u>meq/100 gr.</u>		
	<u>Experimental</u>	<u>Theoretical</u>	<u>Difference</u>
Fe ⁺⁺⁺ , Al ⁺⁺⁺	730	730	
H ⁺	1,372	1,460	- 88
PO4 [■]	2,200	2,190	10

As the foregoing tests dealt with phosphoric acids B prepared in the laboratory, we made sure that crystallisations obtained during production are of the same nature.

Phosphoric acid B. concentration 49.4 % P2O5 - deposit collected during production. (photo 6).

Anions	%	meq/100 gr	Cations	%	meq/100 gr
PO4 [■]	69.7	2,200	Ca ⁺⁺	2.33	116
SO4 [■]	6.47	135	Na ⁺	0.87	38
SiF6 [■]	0.94	13	K ⁺	3.49	90
S ⁻	0.01	0	Fe ⁺⁺⁺	12.89	695
			Al ⁺⁺⁺	0.38	42
			H ⁺	1.367	1,367

Interpretation of analytical results.

	meq/100 gr.		
	<u>Experimental</u>	<u>Theoretical</u>	<u>Difference</u>
Fe ⁺⁺⁺ , Al ⁺⁺⁺	737	737	
H ⁺	1,367	1,474	- 107
PO ₄ ⁼	2,200	2,211	- 11

3) Amount of P2O5 lost in phosphoric acids B.

Phosphoric acid at start (% P2O5)	29.1	38.9	50.5	54.6
Total PO ₄ ⁼ eliminated in the precipitates (milli- equivalents in 4 litres of acid)	18	42	2,620	5,130
PO ₄ ⁼ engaged in the com- pounds of the type (Fe, Al)H ₃ (PO ₄) ₂ (meq/4 litres of acid)		30		
PO ₄ ⁼ engaged in the com- pounds of the type (Fe, Al) (H ₂ PO ₄) ₃ (meq/4 litres of acid)			1,893	3,906
Fe ⁺⁺⁺ + Al ⁺⁺⁺ combined with P2O5 (meq/4 litres of acid)	0	15 Fe ⁺⁺⁺ 1 Al ⁺⁺⁺ 14	631 Fe ⁺⁺⁺ 558 Al ⁺⁺⁺ 73	1,302 Fe ⁺⁺⁺ 825 Al ⁺⁺⁺ 477
Total % P2O5 present in the deposits in relation to the P2O5 contained in the acid	0.03	0.04	1.87	3.28
% of P2O5 present in the deposits combined with iron and aluminium in relation to the P2O5 contained in the acid	0.00	0.03	1.35	2.50

IV. PRECIPITATION PHENOMENON IN CONCENTRATED PHOSPHORIC ACIDS PREPARED FROM TYPE C PHOSPHORIC ACID

1) Physical measurements

Treatment of the acid		Decantation of the 40.4% P ₂ O ₅ acid - 4 hours at 50° C. Elimination of the deposit. Concentration of the clarified acid to 56.1% P ₂ O ₅ . Rest during 48 hours at ambient temperature and centrifugation.	Acid left at rest. Starting hour of decantation at 90° C - 4 - 28 and 100. Quick cooling to 20°. 72 hrs' rest. Elimination of the deposit.
Phosphoric acid % P ₂ O ₅	Density	Total apparent volume of slurry collected. (millilitre/litre of acid.)	% by weight of total deposit with respect to phosphoric acid.
56.1	1.830	235	10.8

2) Amount of P2O5 losses in type C phosphoric acids.

Phosphoric acid % P2O5	40.4	56.1
Density	1.60	1.83
Treatment of the acid	Decantation : 4 hours at 50° C.	Decantation at 90°C after 4 hours - 28 and 100 hours. Quick cooling to 20° - 72 hours of rest and decantation.
Total P ₀₄ [≡] eliminated in the precipitates (milli-equivalents in 4 litres of acid)	1,550	19,600
P ₀₄ [≡] engaged in compounds of the type (Fe,Al) ₂ (P ₀₄) ₂ - meq/4 litres of acid.	1,232	
P ₀₄ [≡] engaged in compounds of the type (Fe,Al) (H ₂ P ₀₄) ₃ - meq/4 litres of acid		11,775
Fe ⁺⁺⁺ + Al ⁺⁺⁺ combined with P ₂ O ₅ (meq/4 litres of acid)	616 { Fe ⁺⁺⁺ 360 Al ⁺⁺⁺ 256	3925 { Fe ⁺⁺⁺ 2280 Al ⁺⁺⁺ 1645
Total P ₂ O ₅ % present in the deposits in relation to the P ₂ O ₅ contained in the acid	1.42	11.3
% of P ₂ O ₅ present in the deposits, combined with iron and aluminium, in relation to the P ₂ O ₅ contained in the acid	1.12	6.8

V. GENERAL CONCLUSIONS

All the acids examined and prepared by the wet process give rise to the formation of solid deposits.

The nature of the latter is determined by the chemical composition of the phosphoric acid considered, and their quantity after a given time depends on the physical conditions of the treatment applied to the acid after its preparation is finished.

In certain deposits one may reveal the presence of calcium sulphate, calcium fluoride, sodium fluosilicate and potassium fluosilicate and, it seems, acid sodium and potassium fluorides. In practice, when precipitates are limited to these salts, they give but little trouble.

It is quite different when the phosphoric acid reaches a certain concentration of P2O5, Fe2O3 and Al2O3. In such cases one finds the presence in the deposits of large quantities of P2O5 combined with iron and aluminium in products like (Fe,Al)H3(PO4)2 or more often than not (Fe,Al)(H2PO4)3.

Type of Phosphoric Acid	% P2O5	% Fe2O3	% Al2O3
A	28.7	0.29	0.88
	46.3	0.42	0.70
B	29.1	0.84	0.54
	38.9	1.10	0.74
	50.5	1.50	0.83
	54.6	1.57	1.04
C	40.4	2.76	1.30
	56.1	3.60	1.60

The iron and aluminium contents steadily increase from phosphoric acid A to phosphoric acid C.

The following table shows that the losses of P2O5 bound with iron and aluminium likewise increase.

Phosphoric Acid		Decantations and filtrations - total time (hours)	Total P2O5 % in the deposits in relation to the P2O5 in the acid	% P2O5 in the deposits (combined with iron or Al) in relation to the P2O5 in the acid.
Type	% P2O5			
A	28.7	336	0.06	0.04
	46.3	384	0.62	0.05
B	29.1	552	0.03	0.00
	38.9	336	0.04	0.03
	50.5	288	1.87	1.35
	54.6	240	3.28	2.50
C	40.4	4(50 ^o)	1.42	1.12
	56.0	204	11.3	6.8

The precipitation phenomena in the phosphoric acids are the cause of certain physical trouble due to the fact that the presence of solid deposits in crystalline forms sometimes lend them great compactness and rather considerable hardness and can thus be a source of difficulties during handling of phosphoric acids with a view to storing them.

When acid iron or aluminium phosphates are present in the deposits, this entails losses due to the structure P2O5 in addition to the impregnation P2O5.

1. Factors which are likely to influence these phenomena favourably

A. How to obtain deposits of suitable crystalline form

The physical condition of a precipitate depends on the speed with which nucleus crystals appear and grow.

Speed with which nucleus crystals appear.

Voimar has introduced the notion of supersaturation and defined it as follows :

Supersaturation (S)

Difference between the total concentration of the substance likely to precipitate (Q) and its solubility in the medium considered (s).

$$S = Q - s$$

In a sufficiently supersaturated solution, small crystals, called nucleus crystals, form spontaneously. If the degree of supersaturation is low, the same phenomenon occurs after a certain time called induction time. In case of weak supersaturation, few nucleus crystals are formed, they grow slowly in size and finally large crystals are obtained. High supersaturations give rise to the formation of many nucleus crystals and lead to the obtaining of many small crystals. When starting from a hot solution, the cooling rate also conditions the state of the precipitate; in the case of substances which are more soluble when hot than when cold, if cooling occurs quickly, the nucleus crystals are numerous and crystals are small; if it occurs slowly, crystals will be larger. By judiciously choosing the speed of cooling, one can in principle cause the formation of a limited number of nucleus crystals and feed them.

Speed with which nucleus crystals grow in size.

This speed is ruled by the law of Noyes-Nernst.

$$V = \frac{D}{L} \cdot A \cdot (Q - s)$$

in which :

V = the rate of growth of nucleus crystals (grams per second)

D = coefficient of diffusion of the substance which crystallizes (square cm per second).

It should be noted that this magnitude is inversely proportional to the viscosity of the solution.

L = thickness of the diffusion layer (centimeters)

A = total surface of nucleus crystals (square centimeters)

Q - s = supersaturation (grams per cubic centimeter)

This leads us, for given agitation speed, temperature and medium, to the following formula :

$$V = K (Q - s)$$

with K = constant.

When nucleus crystals grow in size, two tendencies appear :

a tendency of gathering and one of orientation. If the first tendency prevails, one obtains amorphous precipitates; if the second is predominating, one obtains on the contrary, definitely crystalline precipitates. All these considerations show that it is desirable that crystals form and grow in a weakly supersaturated medium, which will be achieved by a suitable cooling rate and sufficient, but not too violent stirring, in order to prevent destruction of the first crystals, which are always rather fragile.

B. How to obtain minimum loss of P205 in the deposits.

There are two kinds of P205 losses : those due to combined P205 (acid iron or aluminium phosphates) and those due to impregnation P205. If one wishes to reduce to a minimum the combined P205, it is best to precipitate if possible the maximum of iron and aluminium in the form of $(Fe,Al)H_3(PO_4)_2 \cdot 2.5 H_2O$ rather than in the form $(Fe,Al)(H_2PO_4)_3 \cdot 2H_2O$, as the value of ratio $\frac{Fe,Al}{PO_4}$ is more favourable in the first case.

As to the impregnation P205, if one endeavours to obtain deposits made up of crystals of sufficient size, while adhering to the rules of crystallization, it will diminish.

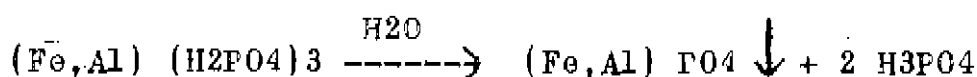
We would also point that, all other things being equal, mechanical treatments, such as decantations, centrifugations and filtrations, give smaller losses by impregnation when carried out hot. This is due to the decrease of the viscosity of phosphoric acid when the temperature rises. One should also avoid as far as possible the presence in the phosphoric acid of any organic matter able to hold P205. When the iron and aluminium content of a phosphoric acid is small, so that precipitation of acid iron and aluminium phosphates is obtained only from a certain concentration of P205 in the acid, one should effect preparation in such a way as to avoid any concentration range in which it is possible to have precipitation with P205 loss.

C) Maximum recovery of the P205 contained in the deposits.

When the combined P205 is engaged in acid iron and aluminium phosphates, one may expect that treatment with water sets free part of this phosphoric acid by hydrolysis. This actually happens. We would mention as an example, a dried slurry from a phosphoric acid obtained from phosphate B and containing, in milliequivalents, in 100 grams :

Fe ⁺⁺⁺	and Al ⁺⁺⁺	599	{ Fe ⁺⁺⁺ 410
			{ Al ⁺⁺⁺ 189
H ⁺		1,200	
PO4 ⁼		1,770	

When dissolving again in water, 972 meq. PO4 ⁼ are put in solution, which corresponds to 82,5 % of the total hydrolysis as per the following formula :



2. Practical conclusions concerning the working of a phosphoric acid plant.

In phosphoric acid production, the aim to be achieved is to reduce iron and aluminium contents of phosphoric acids to values such that precipitations of these ions in the form of acid phosphates have no time to occur to a considerable extent during transportation and handling which takes place from the moment the acid leaves the phosphoric acid plant until it is used.

In general it is possible to separate in the course of concentration of the phosphoric acid a large part of the sulphates, fluosilicates and fluorides which are precipitable, so that in the concentrated acids, the acid iron and aluminium phosphates become the principal components of subsequent deposits. In view of the fact that the greater the supersaturation of the acid with iron and aluminium, the quicker and the more important the precipitation of these salts, one should proceed to one or several cycles comprising a precipitation phase followed by separation of the precipitates formed. Qualitatively, this process could be schematically represented by graph 6.

Industrial preparation of concentrated phosphoric acid by the wet process, from phosphates with high iron and aluminium content should consequently comprise the following operations :

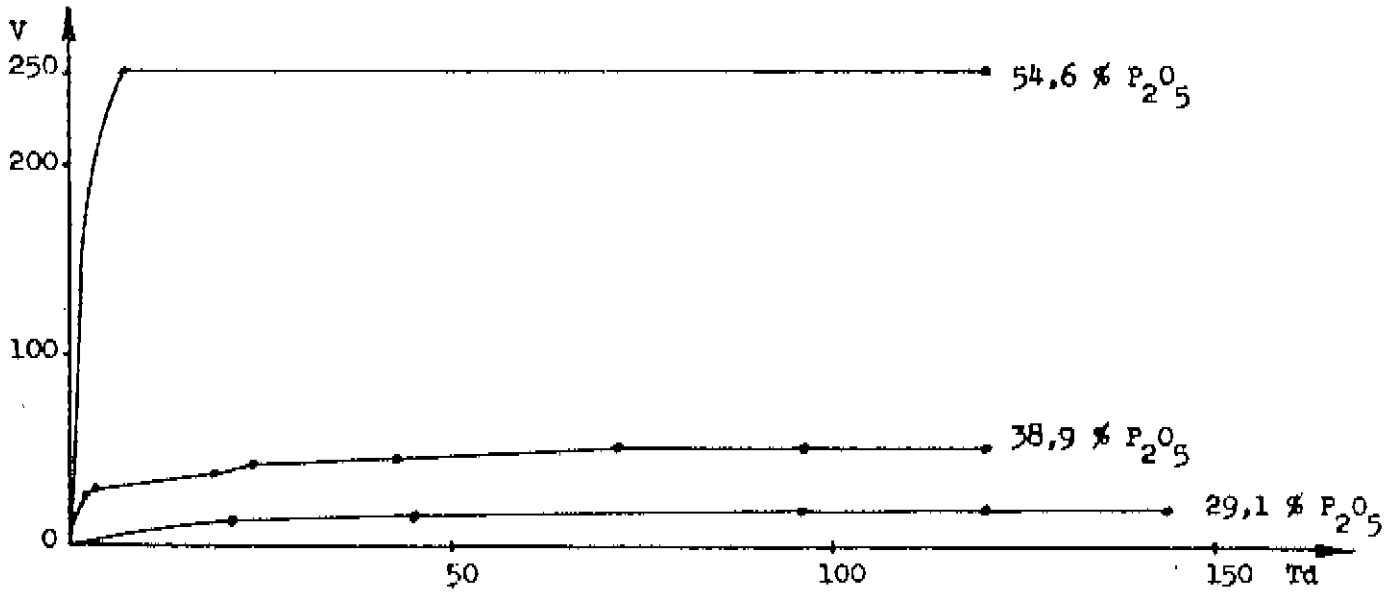
- 1.- In the course of concentration, a decantation made at the maximum possible P₂O₅ concentration which will not result in the precipitation of an undue quantity of iron and aluminium. This decantation aims essentially at separating the abundant precipitates of calcium sulphate, alkaline fluosilicates etc.
- 2.- One or various cycles, comprising :
 - 2a - a precipitation phase consisting of slow cooling in a slightly stirred medium, for the purpose of promoting formation and separation of iron and aluminium phosphates in the form of well-shaped crystals of sufficient size.
 - 2b - a separation operation by centrifugation, centrifugal decantation or centrifuging of the precipitate obtained.
- 3.- Recovery of the P₂O₅ contained in the precipitates, either by incorporating these precipitates with fertilisers to which they are not harmful or by washing them with water intended for return to the production cycle (sulphuric acid dilution water for instance).

Bibliography

- 1.- *Traité de chimie générale* - Pascal - Tome VII - p. 412 (1932)
- 2.- *Traité de chimie générale* - Pascal - Tome VII - p. 414 (1934)
- 3.- *Traité de chimie générale* - Pascal - Tome VI - p. 116 (1934)
- 4.- *The System of Ferric Oxide - Phosphoric Acid - Water.*
A New Phosphate (Sydney Raymond Carter and Norman Holt Hartshorne (2223 - 22 - 33) - J.Chem.Soc. 123 - 2224 - 1923
- 5.- *Complexes involving trivalent Iron and Orthophosphoric Acid - Part III.*
The System Ferric Acid - Phosphoric Oxide - Water at 25°.
R.F. Jameson and J.E. Salmon (23-34) J.Chem.Soc. - 28 - 1954.

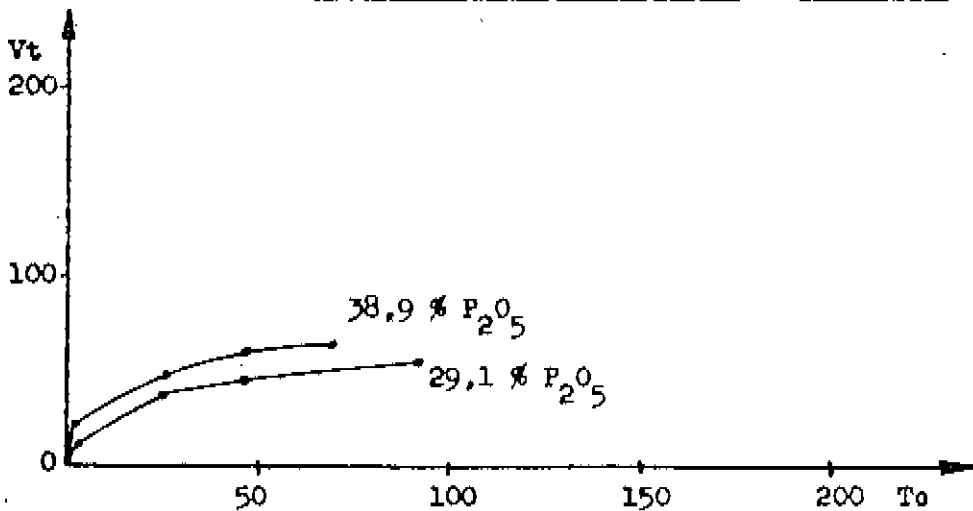
DECANTATION SIMPLE (graphique 1).

SINGLE DECANTATION (graph. 1).



CENTRIFUGATIONS SUCCESSIVES (graphique 2).

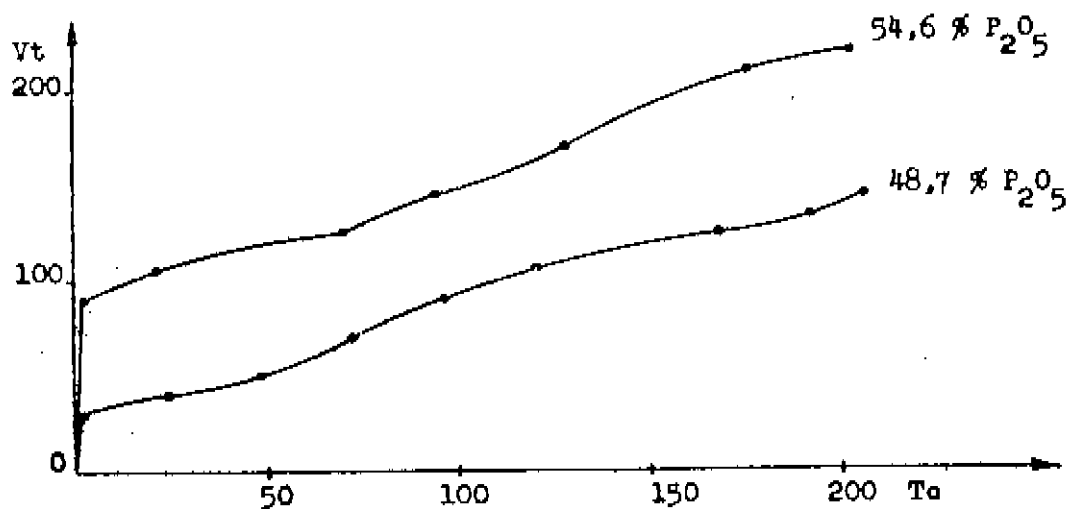
SUCCESSIVE CENTRIFUGATIONS (graph. 2).



- V - Volume apparent du dépôt (ml/l).
Apparent volume of the deposit.(ml/l)
- Td - Temps de décantation (Heures).
Decantation time. (hours)
- Vt - Volume total apparent des dépôts (ml/l).
Total apparent volume of the deposits.(ml/l)
- To - Temps de début de centrifugation. (Heures).
Starting time of centrifugation.(hours)

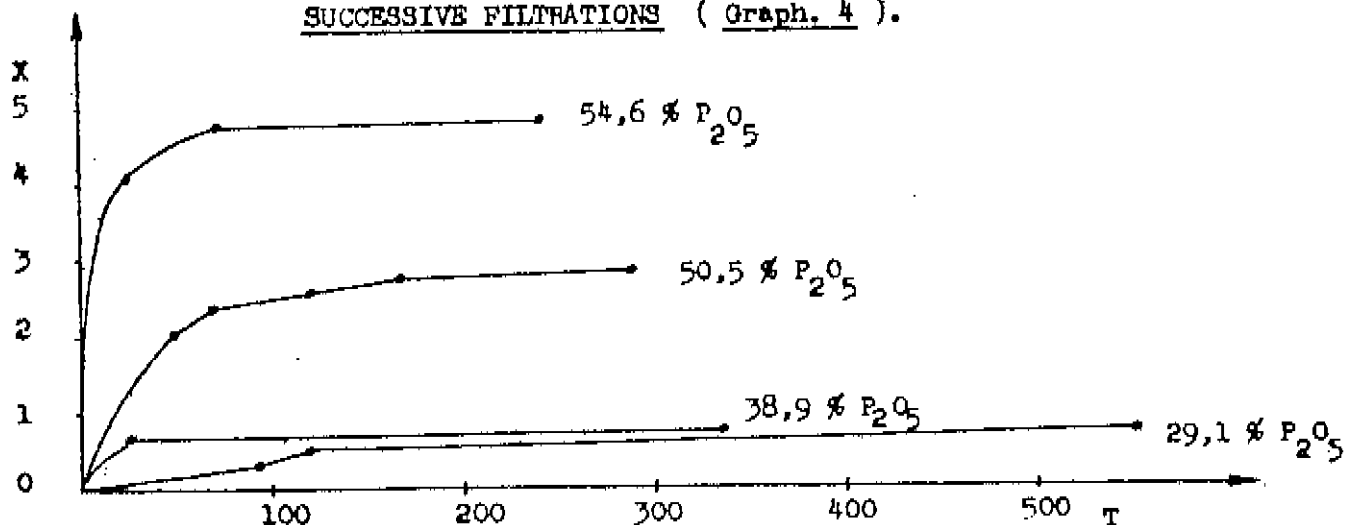
CENTRIFUGATIONS SUCCESSIVES (Graphique 3).

SUCCESSIVE CENTRIFUGATIONS (Graph. 3).



FILTRATIONS SUCCESSIVES (Graphique 4).

SUCCESSIVE FILTRATIONS (Graph. 4).



Vt = Volume total apparent des dépôts (ml/l).
Total apparent volume of the deposits. (ml/l)

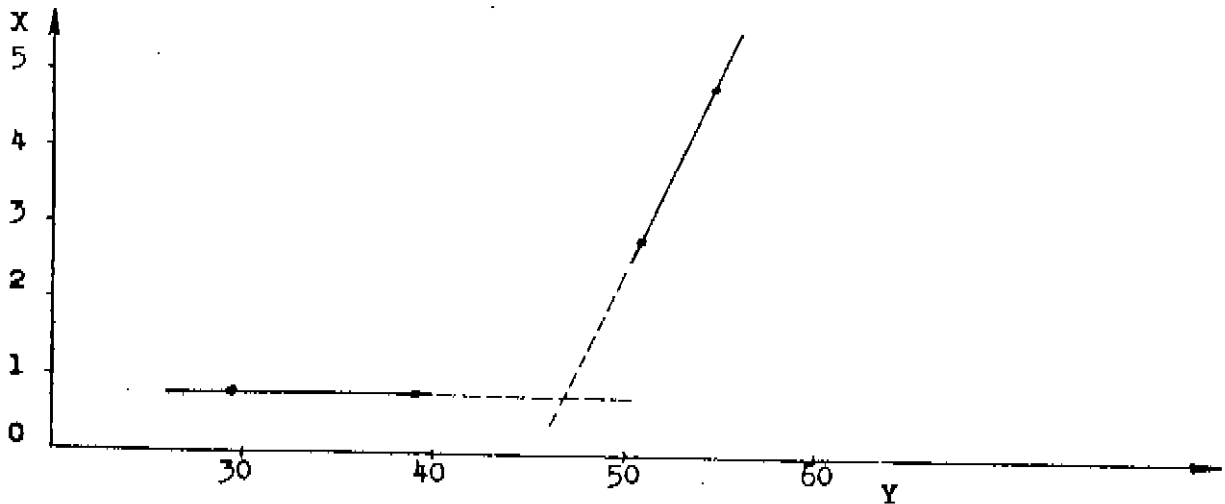
Ta = Temps de début de centrifugation. (Heures).
Starting time of centrifugation. (hours)

X = % total de boue sèche par rapport au poids de l'acide phosphorique de départ.
Total % of dry slurry with respect to the weight of phosphoric acid at start.

T = Temps.
Time.

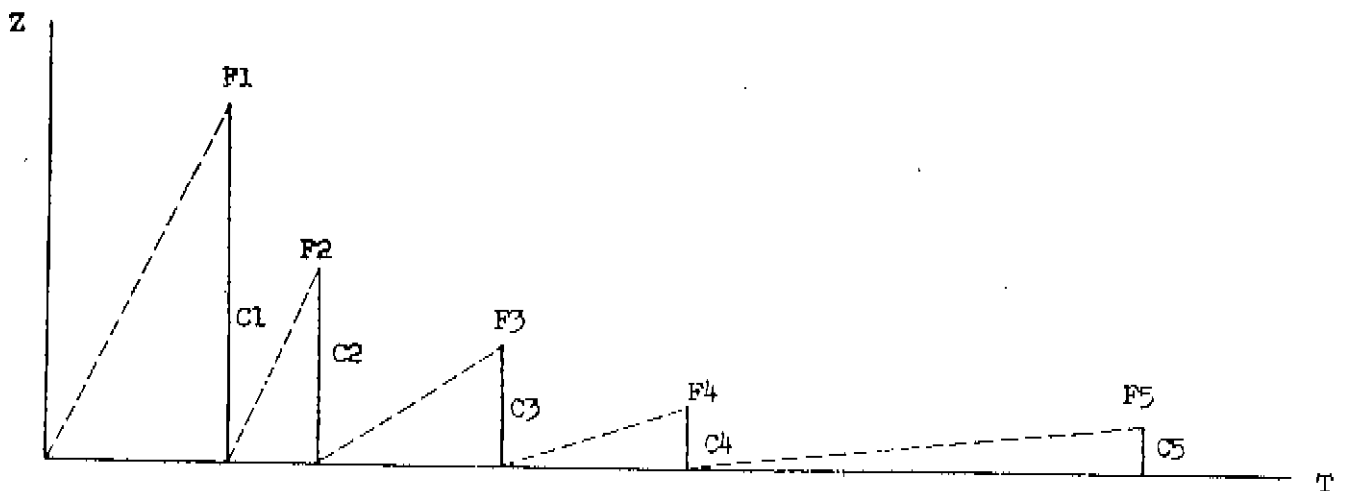
FILTRATIONS SUCCESSIVES (Graphique 5).

SUCCESSIVE FILTRATIONS (Graph. 5).



PRECIPITATION DU FER (Graphique 6).

PRECIPITATION OF IRON (Graph. 6).



X - % total de boue sèche par rapport au poids de l'acide phosphorique de départ.
Total % of dry slurry with respect to the weight of phosphoric acid at start.

Y - % P2O5 de l'acide phosphorique B.
% P2O5 of phosphoric acid B.

Z - Poids de fer précipité par unité de volume d'acide phosphorique.
Weight of iron precipitated per unit of volume of phosphoric acid.

F1-F2-F3-F4-F5 Filtrations.

C1-C2-C3-C4-C5 - Concentrations en fer de l'acide phosphorique après les différentes filtrations.
Iron concentrations of the phosphoric acid after the various filtrations.

T - Temps
Time.

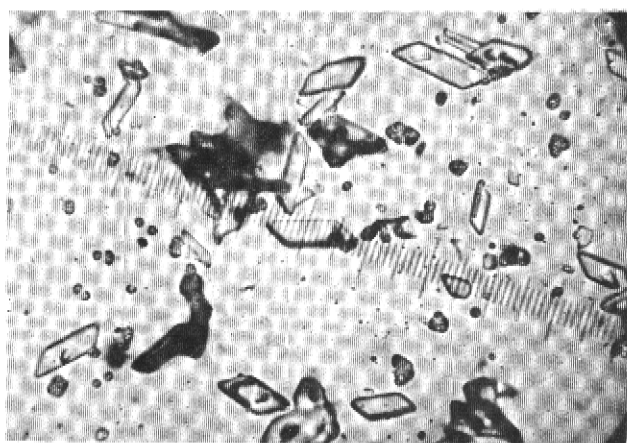


PHOTO I. $\times 250$.

PHOTO I. (magnified 250 times)

I. GYPSE (sulfate de calcium)
Forme clinorhombique.

I. GYPSUM (calcium sulfate)
Clinorhombic shape.

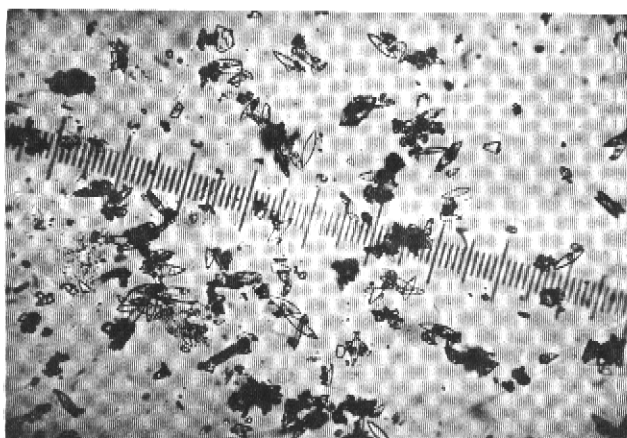


PHOTO II. $\times 250$.

PHOTO II. (magnified 250 times)

II. SULFATE DE CALCIUM.

Formes arrondies dues à des séries de faces en zone.

II. CALCIUM SULFATE.

Rounded shapes due to an infinite number of small faces arranged so as to give the impression of a round shape.

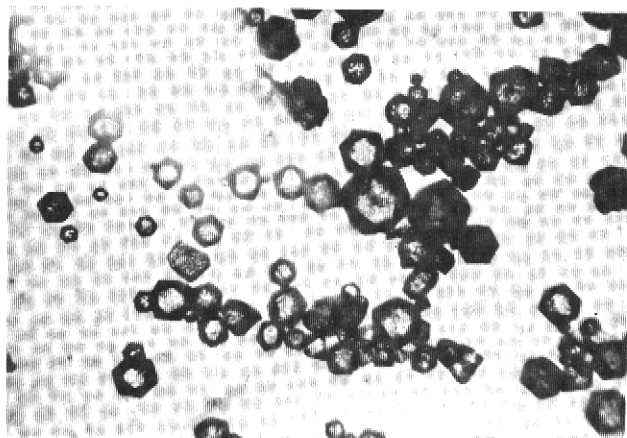


PHOTO III. $\times 450$.

PHOTO III. (magnified 450 times).

III. FLUORURE DE CALCIUM.

Forme octaédrique (empilement de petits cubes - structure polysynthétique).

III. CALCIUM FLUORIDE.

Octahedral shape (pile of small cubes - polysynthetic structure)

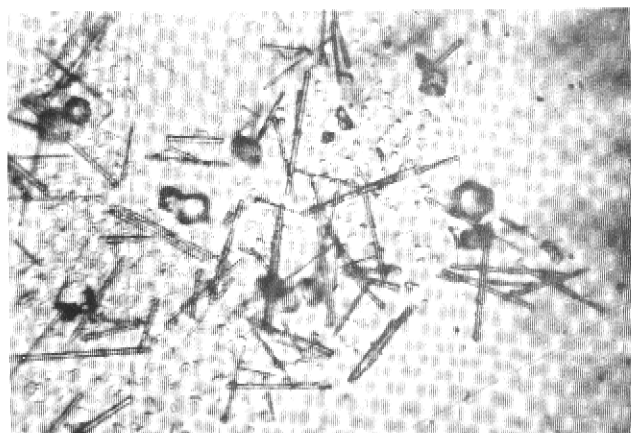
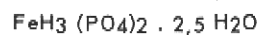


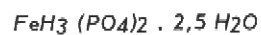
PHOTO IV. $\times 450$
 PHOTO IV. (magnified 450 times).

IV. PHOSPHATE ACIDE FERRIQUE



Forme prismatique à quatre faces terminées par deux pyramides (aiguilles).

IV. FERRIC ACID PHOSPHATE



Prismatic shape with four faces ending in two pyramids (needles)

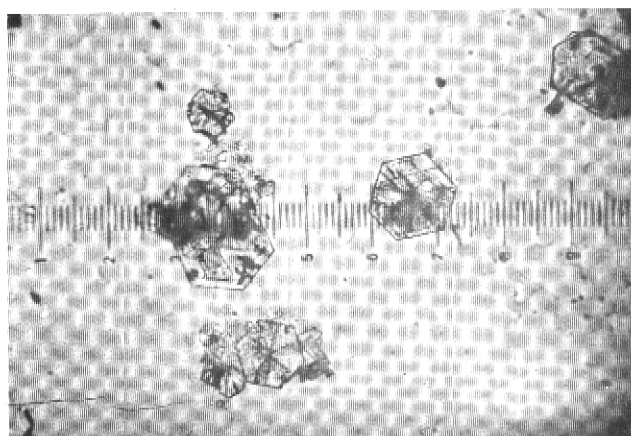
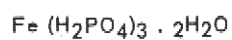


PHOTO V. $\times 250$.
 PHOTO V. (magnified 250 times)

V. PHOSPHATE ACIDE FERRIQUE.



Forme : plaquette hexagonale.

V. FERRIC ACID PHOSPHATE.



Shape : small hexagonal plate.

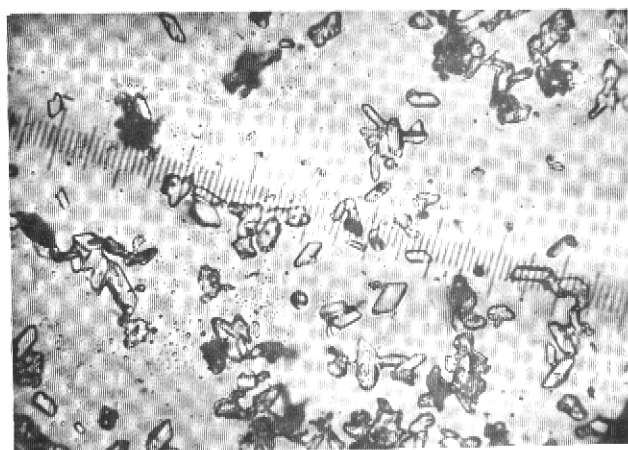


PHOTO 1. $\times 250$.
 PHOTO 1. (magnified 250 times)

1. PRESENCE DE SULFATE DE CALCIUM. (type I.)

1. PRESENCE OF CALCIUM SULFATE (type I).

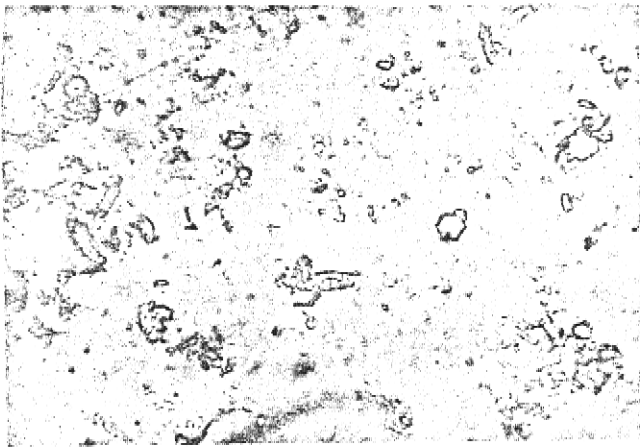


PHOTO 2. $\times 450$
 PHOTO 2 (magnified 450 times)

2. PRESENCE PROBABLE DE DEUX CRISTAUX DE PHOSPHATE ACIDE FERRIQUE.
 (type V).
2. PROBABLE PRESENCE OF TWO FERRIC ACID PHOSPHATE CRYSTALS.
 (type V).

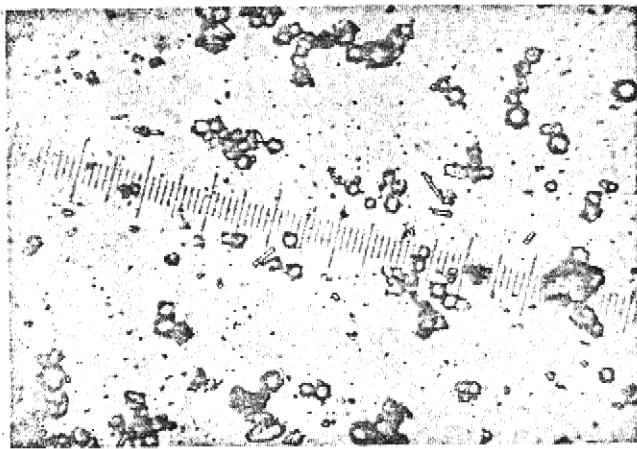


PHOTO 3. $\times 250$.
 PHOTO 3 (magnified 250 times)

3. PRESENCE DE FLUORURE DE CALCIUM.
 (Type III).
3. PRESENCE OF CALCIUM FLUORIDE
 (Type III).

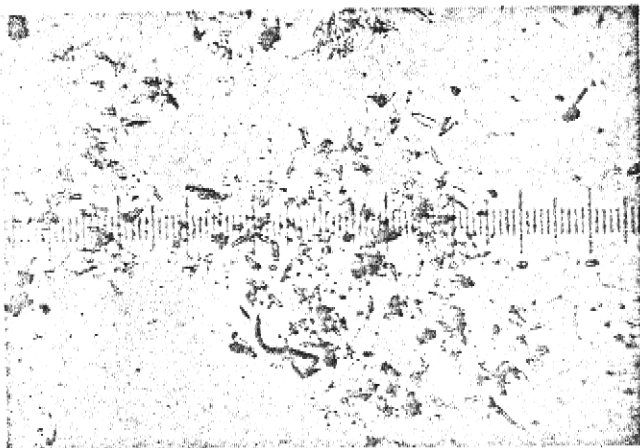


PHOTO 4. $\times 250$.
 PHOTO 4 (magnified 250 times)

4. PRESENCE DE SULFATE DE CALCIUM.
 (type II).
4. PRESENCE OF CALCIUM SULFATE
 (type II).

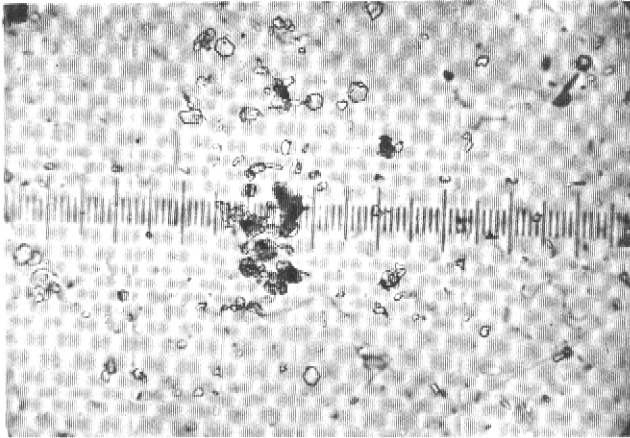


PHOTO 5. $\times 250$.

PHOTO 5 (magnified 250 times)

5. PRESENCE DE PHOSPHATE ACIDE
FERRIQUE.

(Type V).

5. PRESENCE OF FERRIC ACID
PHOSPHATE

(Type V).

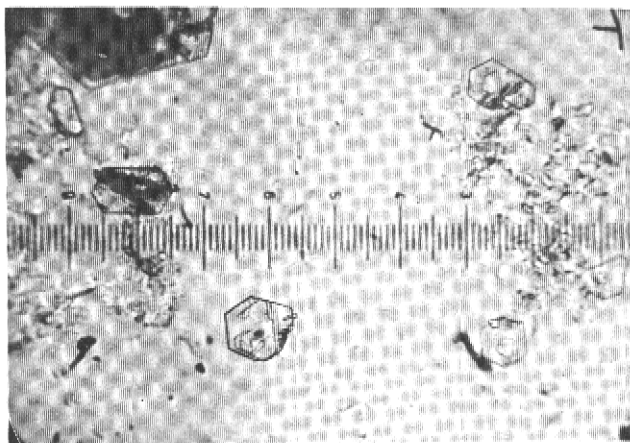


PHOTO 6. $\times 250$.

PHOTO 6 (magnified 250 times)

6. PRESENCE DE PHOSPHATE ACIDE
FERRIQUE.

(Type V).

6. PRESENCE OF FERRIC ACID
PHOSPHATE

(Type V).