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**SIMULTANEOUS PRODUCTION OF MERCHANT GRADE CALCIUM SULPHATE
AND HIGH STRENGTH PHOSPHORIC ACID**

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1. SUMMARY - CONCLUSIONS.

During the past 20 years, raising energy cost and increasing environmental protection regulations have led the fertilizers industry to develop phosphoric acid processes based on recrystallization of calcium sulphate.

Hemi-dihydrate processes, for instance, yield phosphoric acid at more than 40 % P_2O_5 and dihydrate calcium sulphate which can be upgraded to merchant grade by a hydraulic purification.

Conversely, the CENTRAL-PRAYON process yields a medium strength (32 - 35 % P_2O_5) phosphoric acid and calcium sulphate hemihydrate which dries up by mere rehydration with absorption of its own moisture. This process is the less energy consuming when calcium sulphate has to be upgraded.

However, the experience accumulated by PRAYON in controlling the various changes in calcium sulphate crystallization states has made possible to increase the strength of the product phosphoric acid up to 43/45 % P_2O_5 and to obtain calcium sulphate of exceptional purity that, in addition, can be sold, after regular drying, as α hemihydrate, II anhydrite or as a mixture of both.

These two products are in great demand as hydraulic binders thanks to their exceptional mechanical characteristics.

This original combination of high strength phosphoric acid with extremely pure calcium sulphate is achieved by the New Prayon Process PH. 3 (PRAYON HEMIHYDRATE 3 CRYSTALS). In this new process, calcium sulphate is first produced as hemihydrate, converted to dihydrate than reconverted to very pure α hemihydrate or II anhydrite or an α hemihydrate - II anhydrite mixture, in any proportions.

2. PREVIOUS SITUATION AND AIMS OF THE STUDY.

2.1. The Central-Prayon Process :

In the "CENTRAL-PRAYON" phosphoric acid process, calcium sulphate, resulting from the digestion of tricalcium phosphate with sulphuric acid, is first precipitated as dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

After product acid separation, dihydrate is converted to α hemihydrate by increasing the temperature and the acidity.

α hemihydrate is separated by filtration while the mother liquors as well the cake wash filtrate are recycled to the dihydrate attack tank.

Figure 1 shows a simplified flow sheet of the process.

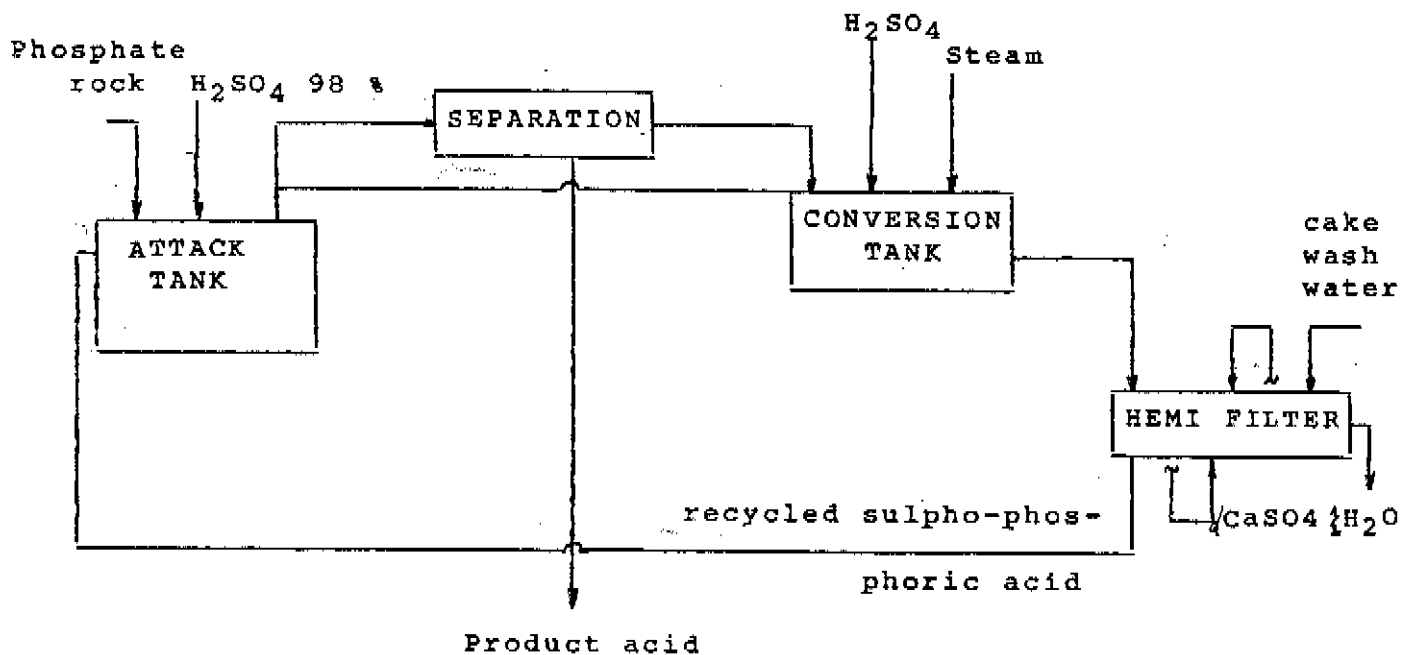


FIGURE 1.

After experimentation in laboratory and pilot plant, this process has been used, for the first time, in our 50 T $\text{P}_2\text{O}_5/\text{d}$ plant in 1965. The capacity has been progressively increased upto 200 T $\text{P}_2\text{O}_5/\text{d}$ in 1970. In 1972, we shut down this unit and converted our old 200 T $\text{P}_2\text{O}_5/\text{d}$ dihydrate plant into a 400 T $\text{P}_2\text{O}_5/\text{d}$ CENTRAL-PRAYON unit.

Incidentally, eleven plants in the world utilize this process which has been used with most commercial phosphate rocks.

When compared to conventional dihydrate route, this process has the following advantages :

- higher P_2O_5 concentration in product acid : 32 - 35 % P_2O_5 .
- low sulphuric acid contamination of the product acid : 1 to 1,5 % H_2SO_4 .
- overall P_2O_5 extraction efficiency higher than 98 %.
- direct production of merchant grade calcium sulphate after a mere line neutralization of the very low residual acidity (less than 0,05 % W.S. P_2O_5 on cake dried at 150 °C).

When compared to usual hemihydrate processes, calcium sulphate produced by the CENTRAL-PRAYON process exhibits two very special characteristics:

- when discharged from the filter, the hemihydrate cake typically contains 20 to 25 % of total water. When allowed to remain on a storage area for about three weeks, without any external interference, the hemihydrate (± 6 % crystal water) reverts to dihydrate (± 20 % crystal water) by absorbing its accompanying moisture.

A completely rehydrated calcium sulphate at ± 5 % moisture is thus obtained. This rehydrated product is dry and has excellent handling properties. For the users (plaster or cement industries), transportation costs are reduced and, during calcination, the amount of water to be evaporated is reduced to about 170 kg of water/ton of $CaSO_4$.

- When discharged from the filter, hemihydrate is under the α hemihydrate crystallization form, contrary to hemihydrate produced by calcination of natural gypsum or phosphogypsum which is under the β hemihydrate form.

This is a marked advantage as α hemihydrate is definitely superior to β hemihydrate as far as mechanical properties are concerned.

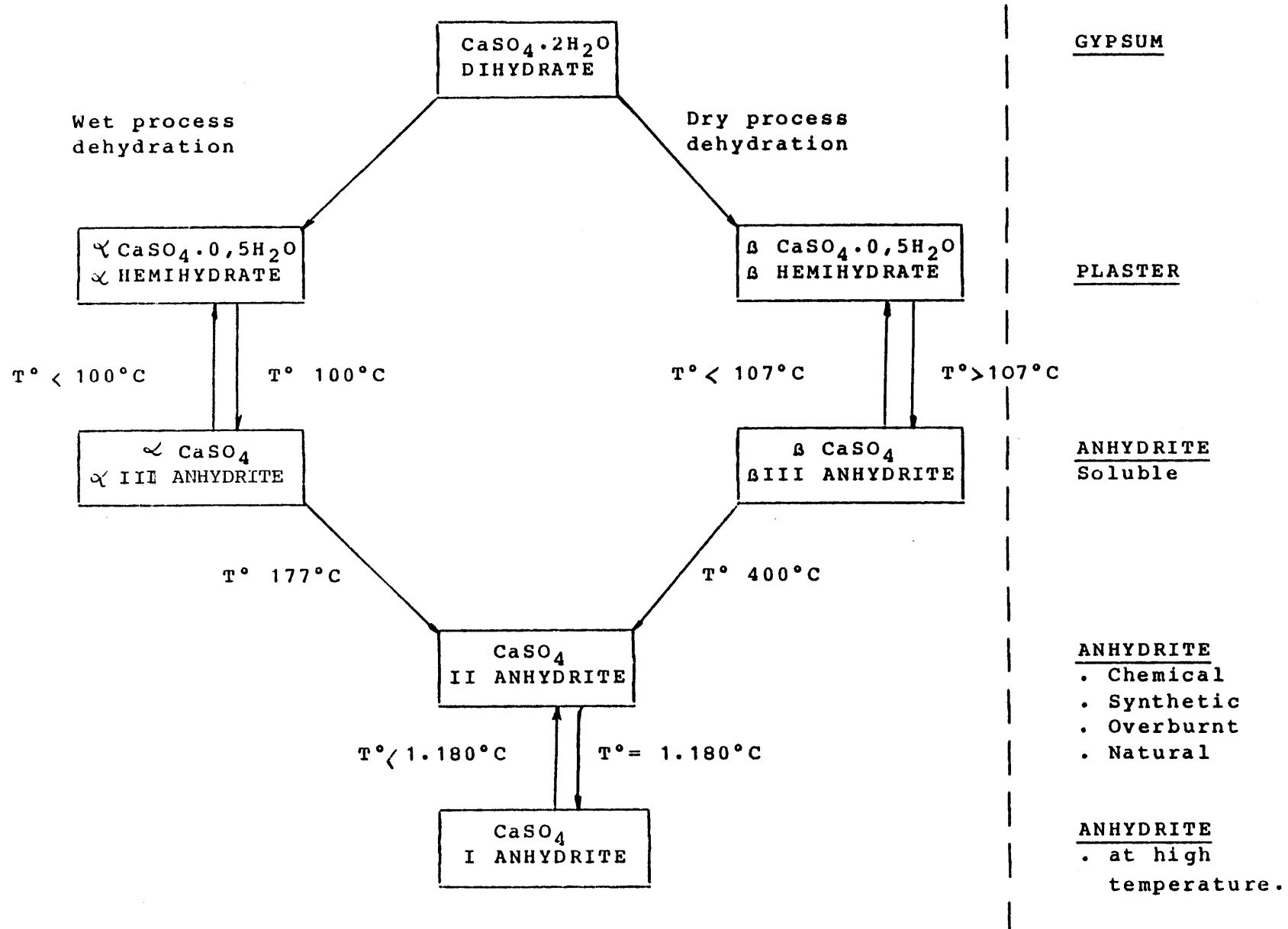
It is worth noting that transforming regular dihydrate into α hemihydrate requires a costly process based on a discontinuous treatment in an autoclave.

However, CENTRAL-PRAYON process does not allow the production of a high P_2O_5 concentration acid : above about 35 % P_2O_5 , gypsum crystals crystallization is affected so that product acid separation becomes difficult and hemihydrate crystallization is impaired.

2.2. Aims of the study :

- We have found interesting to try to develop a phosphoric acid process that would combine "the best of two worlds" : on one side, the direct production of concentrated (more than 40 % P_2O_5) phosphoric acid and on the other side, the production of merchant grade γ hemihydrate either as α hemihydrate or, after natural rehydration, as "auto-drying" phosphogypsum.
- Thanks to the development of the CENTRAL-PRAYON process up to a total reliability stage and its application to the most diversified phosphate rocks -or blends of phosphate rocks- we have accumulated a wide experience in hemihydrate operation as well as in the control of calcium sulphate crystallization changes (dihydrate \rightarrow hemihydrate \leftarrow dihydrate). This experience has been widely relied upon in developing a new process, PRAYON PH. 3 (PRAYON HEMIHYDRATE 3 CRYSTALS) which is going to be described.
- This new process opens wide perspectives in the development of phosphogypsum utilizations. PRAYON PH. 3 P_2O_5 technical efficiency is higher than 99 % and the calcium sulphate (α hemihydrate, II anhydrite or a combination of both) is very pure. These different phosphogypsum qualities are produced at very competitive cost when compared to the "dry mode" production.
- Mechanical properties of the calcium sulphate are directly related to the analysis of the different states of the product.
- For information purpose, the following figure shows the stability zones of the different calcium sulphate crystallization and hydration states as well as the conditions required to transform one hydrated form into another one.

CALCIUM SULPHATE HYDRATION AND CRYSTALLIZATION STATES



Reference : Winfried HÄDRICH und Erwin KAISERSBERGER,
Netsch - Gerätebau GmbH, 8672 Selb./BRD.

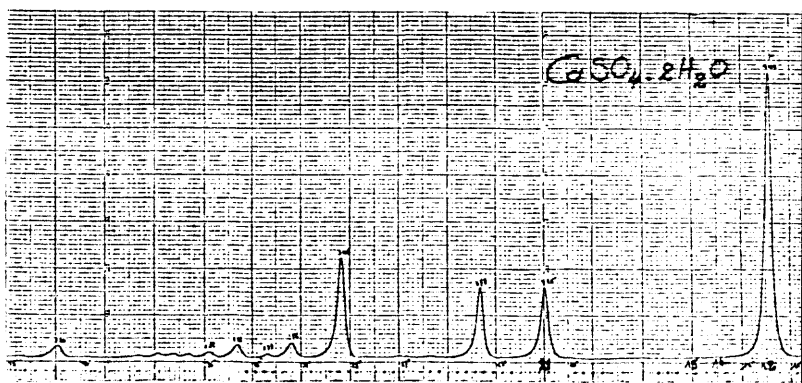
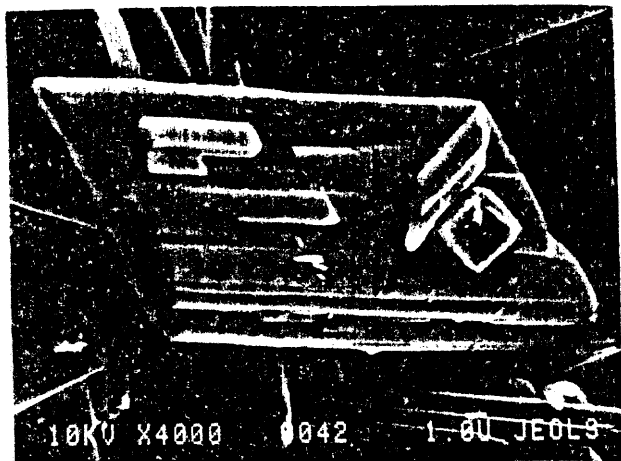
- Au cours de nos études, les techniques analytiques utilisées pour l'identification des phases sont les analyses :
 eau de cristallisation par gravimétrie, spectres de diffraction des rayons X et microscopies électroniques à balayage.

During our research, the following analytical techniques have been used :
 - gravimetry for crystal water determination ;
 - X-ray diffraction ;
 - scanning electronic microscope.

Gypse : $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
 Gypsum :

H_2O crist. = 20 %

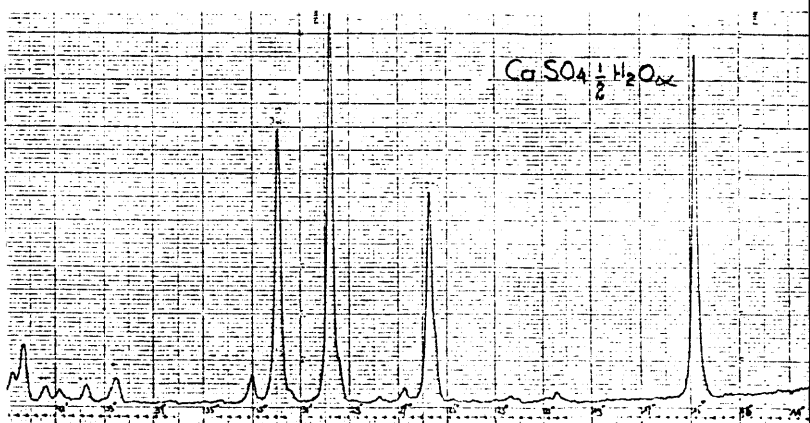
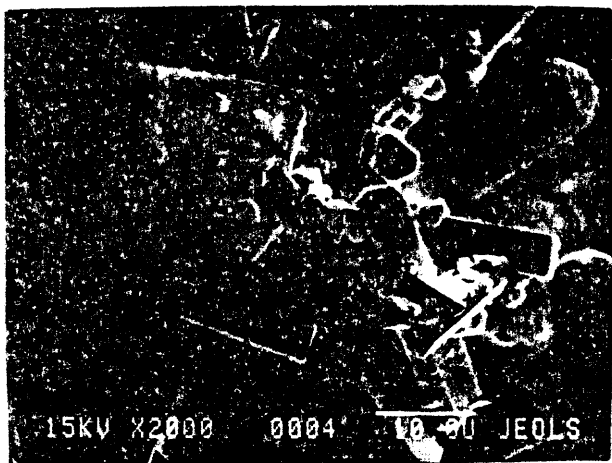
système cristallin prismatique monoclinique
 prismatic monoclinic crystallization system



Hemihydrate α : $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
 α hemihydrate :

H_2O crist. = 5,8 %

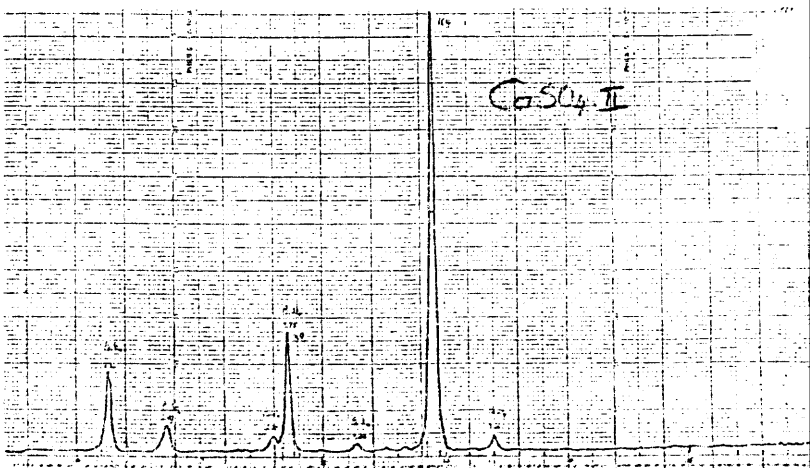
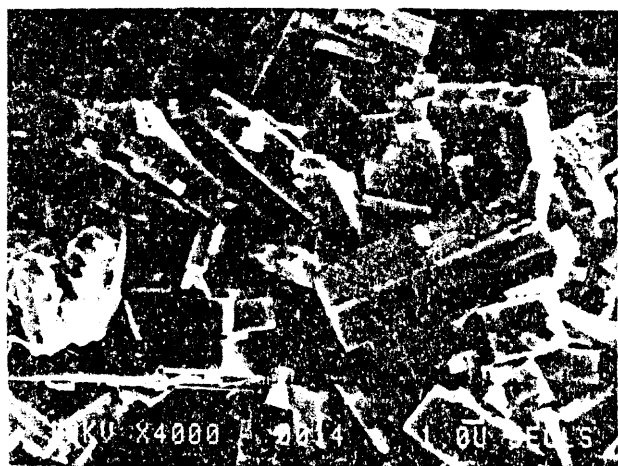
système cristallin hexagonal
 hexagonal crystallization system



Anhydrite II : CaSO_4 II
 II anhydrite :

H_2O crist. = 0,3 %

système cristallin orthorhombique
 orthorhombic crystallization system.



3. PRAYON PH. 3 PROCESS.

Figure 3 shows a simplified flow-sheet of PRAYON PH. 3 process.

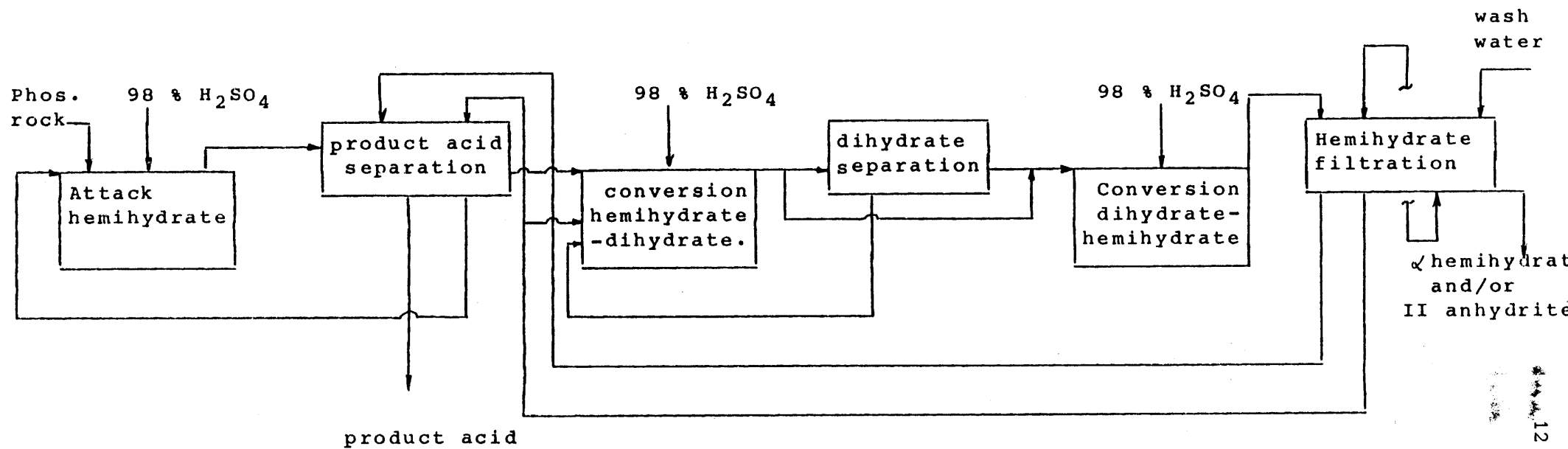


FIGURE 3.

The principle is rather simple :

- During first step, phosphate rock is digested by sulphuric acid in conditions such that a high P_2O_5 strength and superior quality (low solids and impurities content) acid is produced.

Calcium sulphate resulting from this step is a rather impure hemihydrate.

- Acid is separated from hemihydrate by filtration.
- In a second step, thanks to a change of operating conditions (temperature, % P_2O_5 , % SO_4), hemihydrate is recrystallized into dihydrate in order to achieve a first purification, specially in regard to unreacted phosphate rock.
- In the third step, dihydrate is reconverted into hemihydrate, or anhydrite - or a mixture of both - thanks to a new modification of operating conditions. This third step is quite similar to the second part of CENTRAL-PRAYON process and aims at producing a high purity calcium sulphate which is separated by filtration and washed with water.
- In each step, the operating conditions are modified either by external interference (cooling, sulphuric acid or steam addition) or by an adequate and controlled recycling of the various filtrates.

4. PILOT TESTS.

4.1. Aims :

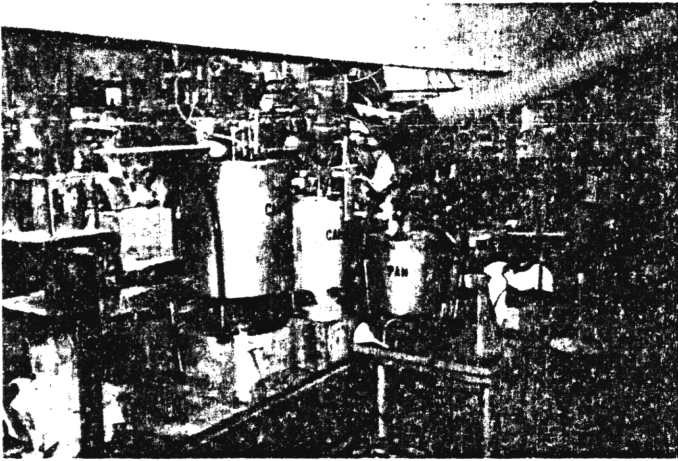
Following some discontinuous laboratory tests, a pilot plant has been built and started early '83 in order to :

- verify the feasibility of the process.
- define all operating parameters on the operation and on the quality of the products.
- establish material, energy and main impurities balances.
- study the stability of the process, specially the evolution of the various calcium sulphate hydration forms during shut downs and process upsets.
- study the influence of residence time in the various vessels.
- determine the filtration characteristics of the various products.
- establish the main sizing criteria for an industrial size plant based on PH. 3 process.

4.2. Pilot equipment (photos 1 to 5)

- Capacity of the pilot plant is ± 20 kg P_2O_5 /24 hours based on our former experience, a larger capacity pilot plant will not give better information but, on the opposite side, handling of raw materials, intermediate and final products becomes a burden on the operators and distract them from the operation control.
- The installation is basically made of agitated 20/25/5 stainless steel vessels. The agitators are a copy, in reduced size, of our industrial agitators. In all vessels, temperature is kept constant at the desired set point either by heating plates or by water-jacket coolers.
- All reagents are introduced in a continuous and controlled way, either by continuous weighing for the solids or by metering pumps for the liquids.
- Filtration operations are discontinuous and performed on a buchner type filtering cell. Slurry to be filtered is however taken continuously as well as filtrates to be recycled.
- The operation is continuous (one technician and two skilled operators per shift) five days a week. The operators run themselves the physical and analytical determinations necessary for the control of the operation while the shift composite samples are analyzed by the central lab.

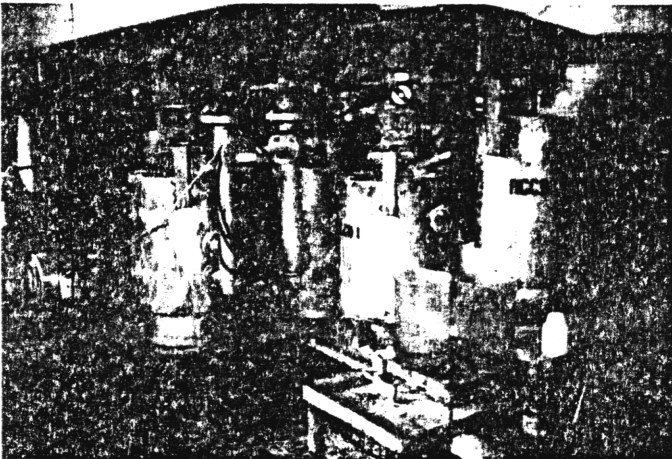
PILOT PLANT EQUIPMENTS.



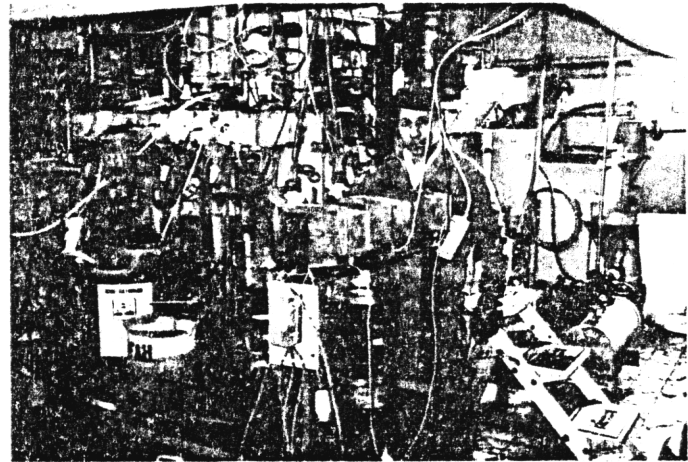
1. Section d'attaque et de production d'acide à haut titre.
1. Hémihydrate attack section.



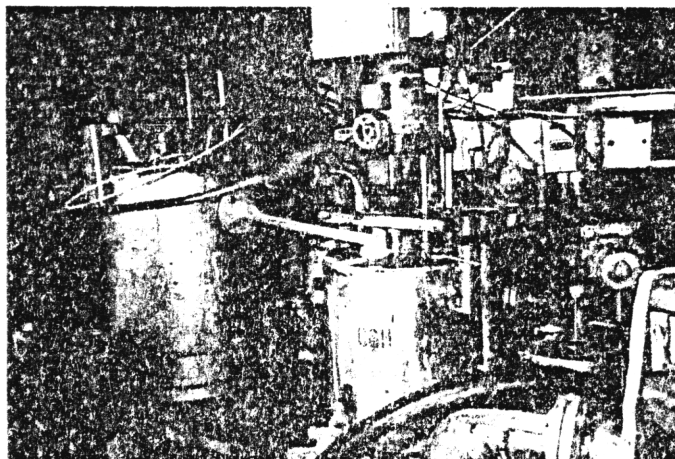
2. Une cellule de filtration.
2. Filtering cell.



3. Section de conversion hémihydrate α - dihydrate
3. α hemihydrate - dihydrate conversion section.



4. Dosage et recyclage en continu
des réactifs.
4. Continuous feeding and recycling
of the reagents.



5. Section de conversion
dihydrate - hémihydrate α
(et/ou) anhydrite II.
5. Dihydrate - α hemihydrate
or dihydrate - II anhydrite
conversion section.

4.3. Tests and results.

4.3.1. Test performed and scheduled :

Several 4 weeks testing periods were performed during 1983 and 1984.

During the initial periods, a blend of KOLA/CASA phosphate rocks, similar to the one used in our Engis plant, was tested. Afterwards, a blend KOLA/BU CRAA, CASA and FLORIDA rocks have been tested. Two more testing periods on KOLA rock are scheduled for the end of this year.

Analytical results presented in this paper refer to tests on blends KOLA/CASA (ratio 68/32 based on dry phosphate weight) and KOLA/BU CRAA (ratio 50/50 based on dry phosphate weight). Only the conclusions and final results will be presented. Initial results as well as intermediate tests will be omitted.

4.3.2. Tests results :

- Step one : hemihydrate attack and filtration :

production of 40 - 45 % P_2O_5 acid with low free SO_3 (± 1 %) has been obtained without any major difficulty ; however, more difficult has been the control of operating conditions allowing the production of hemihydrate which would filter rapidly and would lend itself to a complete rehydration during the second step.

Since the beginning of the test, it has been clearly demonstrated that the P_2O_5 content of the liquid phase during the second step of the process (rehydration of hemihydrate into dihydrate) has a definite influence on the degree of rehydration. Consequently, it is very important to avoid any uncontrolled P_2O_5 transfer from step one to step two.

These uncontrolled transfers may be due to a poor hemihydrate crystallization, which would cause a poor filtration, or to an incomplete phosphate rock digestion, which would cause high unreacted and co-crystallized P_2O_5 content in the hemihydrate. (Most part of this P_2O_5 would be solubilized during rehydration).

These initial difficulties have been rapidly overcome by :

- an internal modification of the hemihydrate attack section so as to digest the rock in a progressive manner and to produce a hemihydrate perfectly constant in composition and stable.
- an appropriate routing of the liquids recycled from the next steps so as to be able to perfectly control SO_3 and P_2O_5 contents during each steps of the process.

- Step two : conversion hemihydrate-dihydrate :

As mentioned above, during the initial test period, the completeness of rehydration has been rather difficult to control. Here again, the problem has been solved by an internal modification of the rehydration volume and a proper control of the operating conditions by recycling the liquors from the other steps.

- Step three : conversion dihydrate-hemihydrate-hemihydrate filtration :

This step is exactly similar to the second step of the CENTRAL-PRAYON process so that no special difficulty was expected.

The only problem that has occurred has been the impossibility to obtain the required hemihydrate purity when rehydration is not complete during the second step of the process.

In this case, hemihydrate produced during the first step is directly transferred, without recrystallization, to the third step. As this hemihydrate has not been produced in optimum conditions (high P_2O_5 and low SO_3), its poor crystallization will affect the filtrability of the final product and the latter will be polluted by its impurities (mainly P_2O_5). This problem has completely disappeared as soon as the rehydration process during the second step has been under total control.

One interesting phenomenon which appeared during the tests is the possibility to obtain II anhydrite instead of α hemihydrate by modification of the operating conditions during step three. When operating with intermediate conditions, it has also been possible to produce a mixture of II anhydrite and α hemihydrate and to adjust, at will, the ratio of each component. Calcination of II anhydrite requires less water to evaporate. An additional advantage is that the presence of a certain amount of II anhydrite enhances the mechanical properties of α hemihydrate.

Table III shows the effect of granulometry, percentage of II anhydrite and ratio W/P (water/product) on the mechanical properties of the final product.

Other information resulting from the pilot tests :

- in addition to the production of high P_2O_5 concentrated product acid and high purity calcium sulphate, the pilot tests have made possible to work out the material, energy and chemical balances. These balances show that :
- when producing 40-45 % P_2O_5 acid, overall P_2O_5 recovery is 99 to 99,5 %.
- similarly to most high strength processes, product acid impurities level is much lower than dihydrate acid of the same P_2O_5 concentration. This is of course an advantage for the users but also, precipitation and scaling during storage and concentration will be reduced.
- fluorine evolution per unit of P_2O_5 is appreciably higher than for a conventional process. This allows to recover more fluorine and to increase the concentration of the recovered fluosilicic acid solution.

It should be mentioned that for certain types of rock tested, active silica has been added to one or several steps of the process in order to make up for the active silica rock deficiency. In all cases, this addition has improved the crystal shape of the various calcium sulphate and has increased their time-stability. It is worthnoting that, as far as hemihydrate is concerned (first and third step), silica addition has allowed to obtain hemihydrate at a definetely lower temperature with, as a consequence, a sensible reduction of the corrosion of the equipments.

4.3.3. Table I - Operating conditions.

DESIGNATION	KOLA/CASA (68/32)	KOLA/BU CRAA (50/50)
1. <u>Sept one : hemihydr attack & filtration</u>		
. product acid % P ₂ O ₅		42 to 45 %
. temperature °C	85	75
. excess SO ₃ gr/l		10 to 15 gr/l
. % solids		26 to 28 %
. reaction volume m ³ /t P ₂ O ₅ x 24 h	1	1,5
. filtration coefficient : t P ₂ O ₅ /24 h x m ²	3,5	4
2. <u>Step two : conversion hemi.-dihydrate</u>		
. % P ₂ O ₅ liquid phase	18 to 23	20 to 26
. temperature °C		45 to 50 °C
. excess SO ₃ gr/l	3 to 5 %	5,5 to 6,5
. % solids		45 to 50 %
. rehydration volume m ³ /t P ₂ O ₅ x 24 hours	2,5	3
3. <u>Step three : conversion dihydrate - hemihydrate and hemi. - filtration</u>		
. % P ₂ O ₅ in liquid phase	24	26
. temperature °C	82	90
. % H ₂ SO ₄	8,5	9,5
. % solids	24	26
. conversion volume m ³ /t P ₂ O ₅ x 24 h		0,5
. filtration coefficient : t P ₂ O ₅ /24 h x m ²		6,2 à 6,7

Remark : for II anhydrite production, conditions are :
 % P₂O₅ : 17 to 20 % ; Temp. °C : 70 to 75 °C ; % H₂SO₄ : 19 to 25 %.

4.3.4. TABLE II - Treatment of various phosphates rocks per the PH.3. process
Chemical analysis.

DESIGNATION	PHOSPHATES KOLA/CASA (68/32)				PHOSPHATES KOLA/BU CRAA (50/50)					
	Phosphate blend	Product acid	calcium sulfate		Phosphate blend	Product acid	Calcium sulfate			
			α hēmi. as such	II anhyd. as such			α hēmi. as such	α hēmi + 20 % II, as such	II anhyd. as such	
specific gravity kg/dm ³		1511				1485				
total H ₂ O	1 on dry bas. 100°C		21,4 on dry basis	35 250 °C	0,8		17,8	21,3	32	
H ₂ O 50-250 °C			5,6	0,6			6,1	5,2	0,3	
P ₂ O ₅ T	37,06	44,7	0,19	0,40	37,8	42,7	0,31	0,21	0,40	
CaO	50,2	0,14	39,8	38,5	51,9	0,073	38,4	38,4	39,4	
SO ₃	1,14	1,5	58,3	56,5	0,56	1,7	57	57,3	58,1	
F	3,5	1,6	0,011	0,08	3,6	1,6	0,13	0,04	0,06	
SiO ₂	1,9	0,6	0,9	1,2	2,4	0,8	2,1	1,7	0,6	
Al ₂ O ₃	0,69	0,54	0,095	0,079	0,60	0,56	0,13	0,10	0,094	
Fe ₂ O ₃	0,44				0,33	0,46	0,039	0,034	0,022	
Na ₂ O	0,36				0,33	0,018	0,11	0,088	0,13	
K ₂ O	0,10				0,11	0,004	0,029	0,022	0,023	
MgO	0,18				0,10	0,11	0,013	0,006	0,008	
Ct	0,50				0,34	0,02	0,03	0,04	0,06	
U ₃ O ₈	0,006	0,005	< 0,002	< 0,001	0,0045	0,0047	< 0,0001	0,0005	0,0004	
-										

4.3.5. MICROSCOPIES ELECTRONIQUES A BALAYAGE DES SOLIDES AUX 3 ETAGES
 4.3.5. ELECTRONIC MICROSCOPE SCANNING OBSERVATION OF THE SOLIDS PRODUCED DURING THE THREE DIFFERENT STEPS

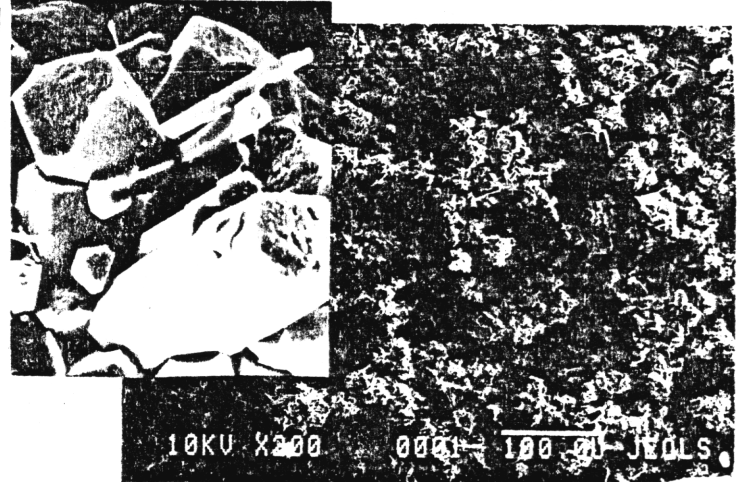
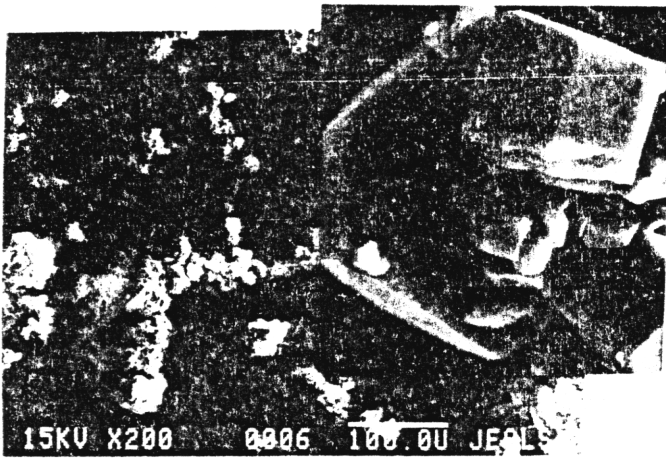
1.- ATTAQUE HEMIHYDRATE
 1.- STEP ONE - HEMIHYDRATE REACTION

KOLA/CASA (68/32)

Acide produit : P_2O_5 : 42,8% ; SO_3 : 0,6 %
 Product acid : P_2O_5 : 42,8% ; SO_3 : 0,6 %

KOLA/BU CRAA (50/50)

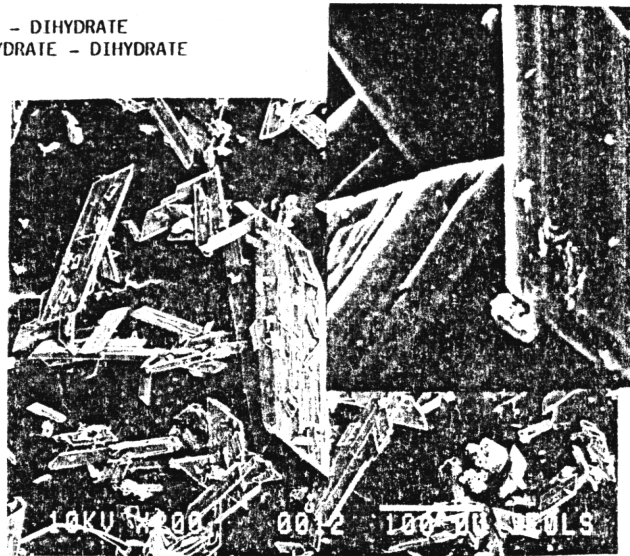
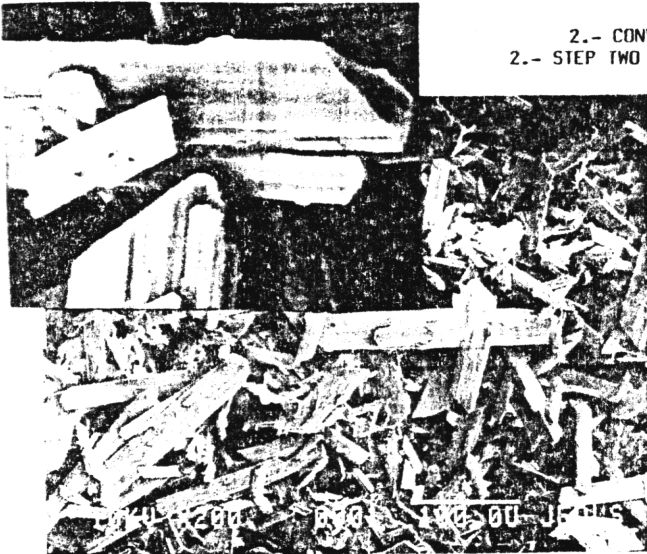
Acide produit : P_2O_5 : 43,2 % ; SO_3 : 1,6 %
 Product acid : P_2O_5 : 43,2 % ; SO_3 : 1,6 %



H_2O C : 6,8% ; P_2O_5 TOT : 1,5% ; P_2O_5 SET : 1,2 %

H_2O C : 6,6 % ; P_2O_5 TOT : 1,7 % ; P_2O_5 SET : 1,5 %

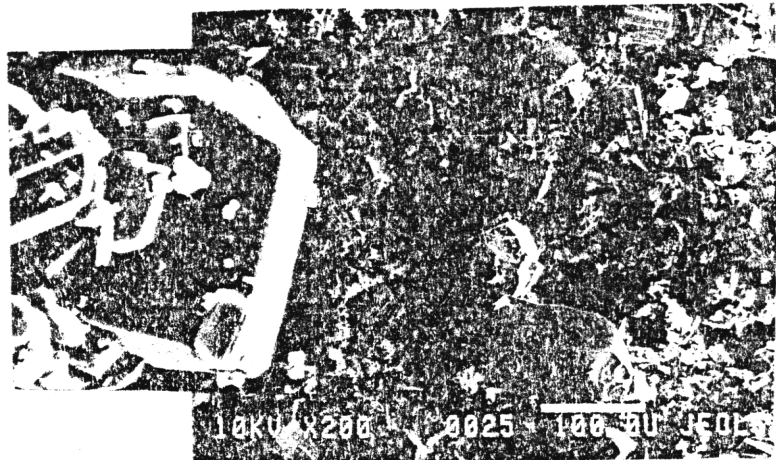
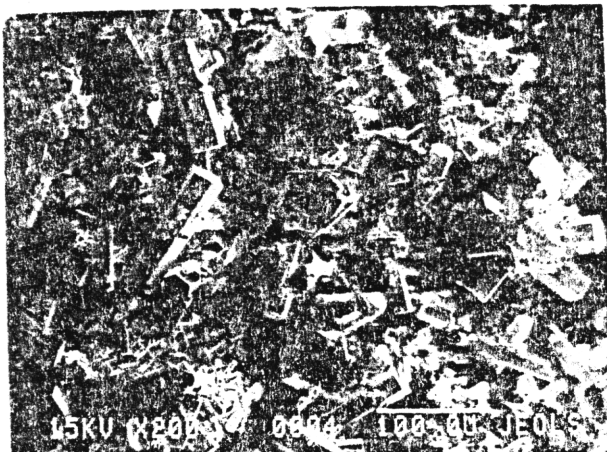
2.- CONVERSION HEMIHYDRATE - DIHYDRATE
 2.- STEP TWO : CONVERSION HEMIHYDRATE - DIHYDRATE



H_2O C : 18,7 % ; P_2O_5 TOT : 0,58 % ; P_2O_5 SET : 0,38 %

H_2O C : 19,2 % ; P_2O_5 TOT : 0,37 % ; P_2O_5 SET : 0,2 %

3.- CONVERSION DIHYDRATE - HEMIHYDRATE
 3.- STEP THREE - CONVERSION DIHYDRATE - HEMIHYDRATE



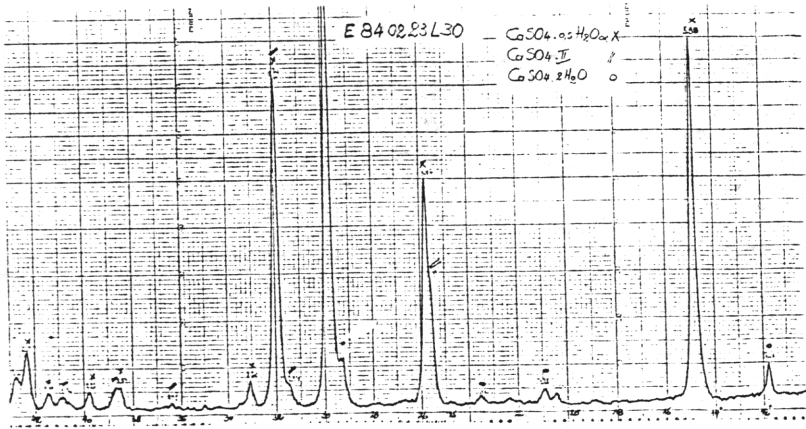
H_2O C : 5,5 % ; P_2O_5 TOT : 0,16 % ; P_2O_5 SET : 0,03 %

H_2O C : 5,6 % ; P_2O_5 TOT : 0,21 % ; P_2O_5 SET : 0,10 %

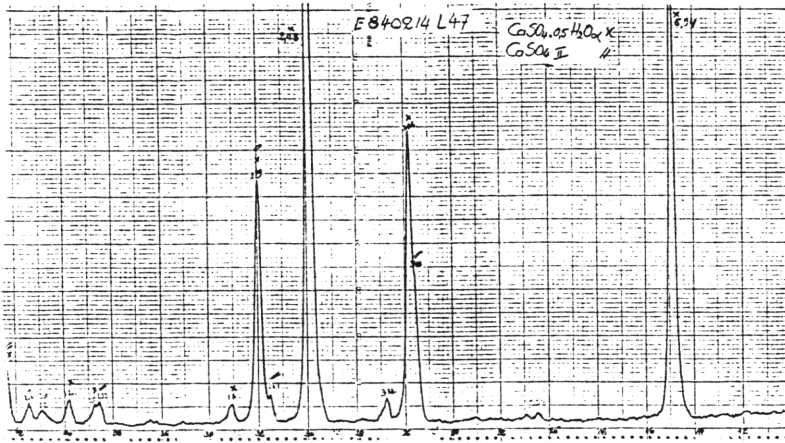
4.3.6. MICROSCOPIES ET SPECTRES DES RAYONS X DES SULFATES DE CHAUX PRODUITS
(HEMI α + ANHYDRITE II).

4.3.6. MICROSCOPIC DETERMINATION AND X-RAY DIFFRACTION ANALYSES OF CALCIUM SULFATE PRODUCTS
(α HEMIHYDRATE AND II ANHYDRITE).

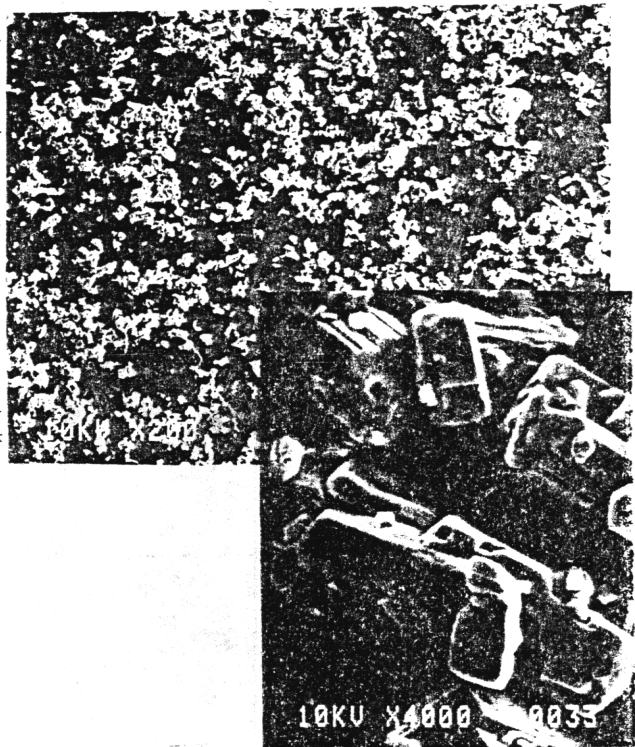
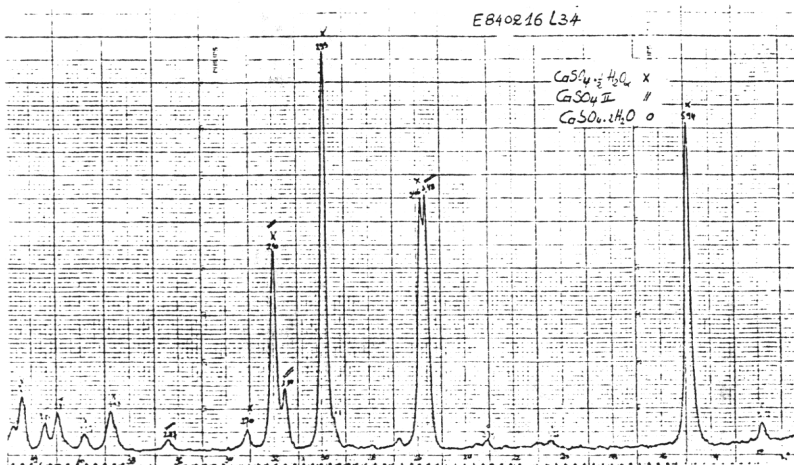
E. 84.03.23L30 : H₂O C = 5,9 ; P₂O₅ TOT : 0,35 % ; P₂O₅ SET = 0,22 %
W.S.



E. 84.02.14L47 : H₂O C = 5,5 ; P₂O₅ TOT = 0,17 ; P₂O₅ SET = 0,10 %
W.S.



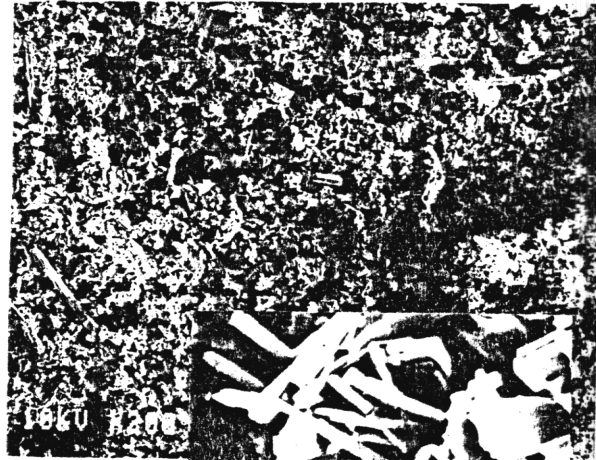
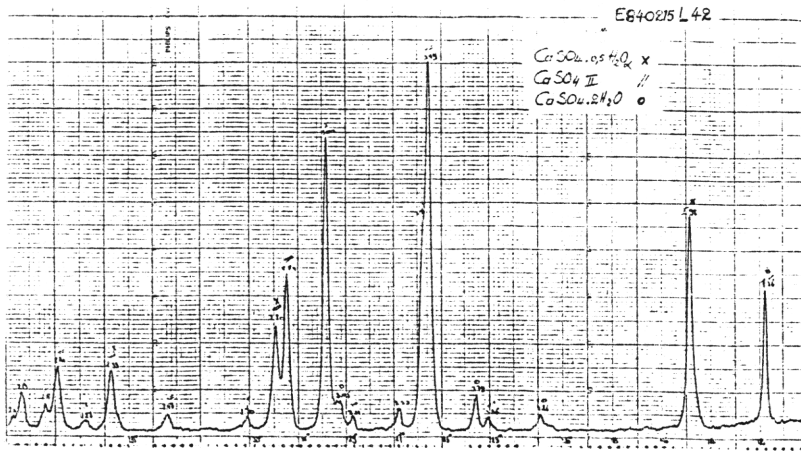
E. 84.02.16L34 : H₂O C = 4,9 ; P₂O₅ TOT = 0,32 ; P₂O₅ SET = 0,25 %
W.S.



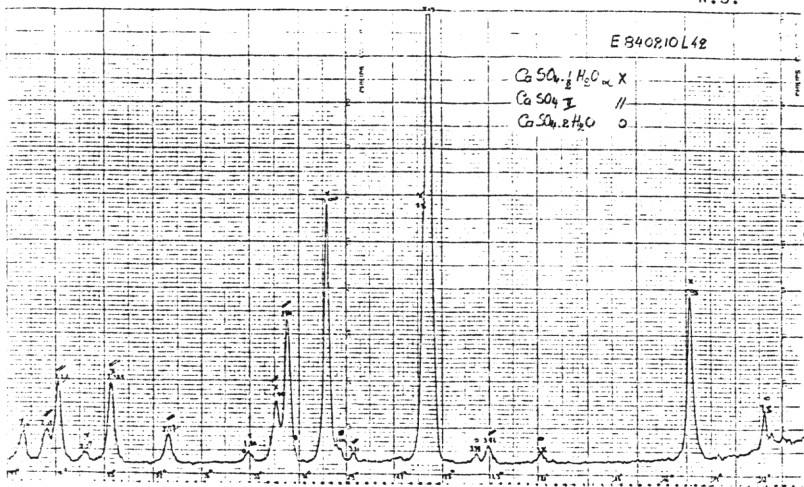
4.3.6. (SUITE) MICROSCOPIES ET SPECTRES DES RAYONS X DES SULFATES DE CHAUX PRODUITS
(HEMI & ANHYDRITE II).

4.3.6. (CONTINUED) MICROSCOPIC DETERMINATION AND X-RAY DIFFRACTION ANALYSES OF CALCIUM SULPHATE PRODUCTS
(< HEMIHYDRATE & II ANHYDRITE).

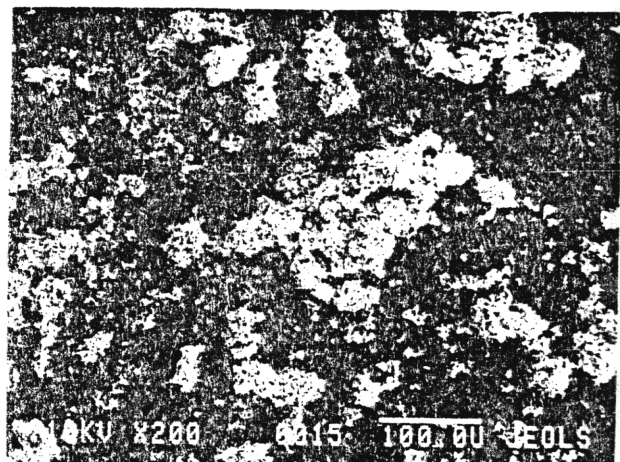
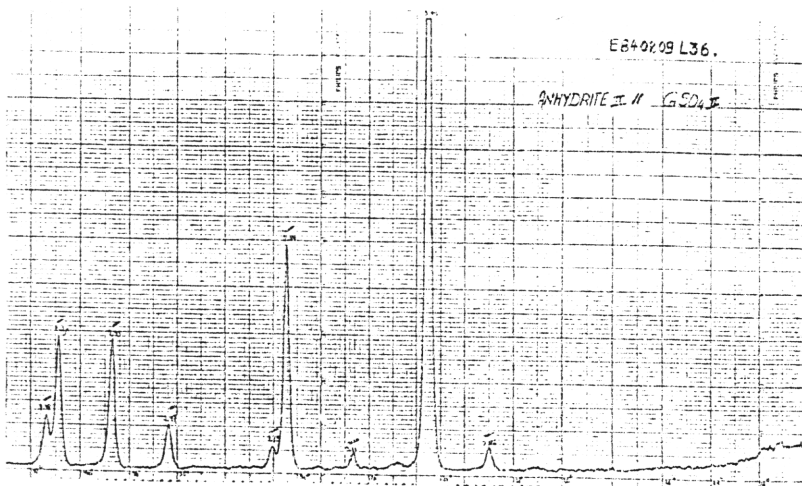
E. 84.02.15L42 : $H_2O C = 4,3 \%$; $P_2O_5 \text{ TOT} = 0,42 \%$; $P_2O_5 \text{ SET} = 0,34 \%$
W.S.



E. 84.02.10L42 : $H_2O C = 2,5 \%$; $P_2O_5 \text{ TOT} = 0,35 \%$; $P_2O_5 \text{ SET} = 0,19 \%$
W.S.



E. 84.02.09L36 : $H_2O C = 0,4 \%$; $P_2O_5 \text{ TOT} = 0,31 \%$; $P_2O_5 \text{ SET} = 0,16 \%$
W.S.



SAMPLE (hemihydrate and/or II anhydrite)	Treatment A such : A.S. Alcohol washed : A.W. Ground : G.R.	Chemical analysis						Physical analysis				Strength test														DEN- SITE	
		pH 10 %	cris water	on dry basis 250°C				Blaine cm ² /gr	Cumulat. seive anal				E/P	Bending kg/cm ²						Compression kg/cm ²							
				P ₂ O ₅ Tbt.	CaO	SO ₃	F		+63μ	+45μ	+32μ	+20μ		1 h	3 h	5 h	1 d	7ds	28ds	1 h	3 h	5 h	1 d	7 ds	28 ds		7 ds
83.10.04 KOLA/CASA (68/32)	A.S. + G.R.	-	3,7	0,31	39	58,1	0,061	5190						0,3	19	-	28,8	37,5	43,9	42	53	-	70,4	153	222,8	385	
83.10.04 KOLA/CASA (68/32)	A.S. + G.R. + 0,4 % CaO	-	-	-	-	-	-	-						0,3	28	-	63,2	59	-	96	135	-	263,2	359	-	428	
84.05.25 II KOLA/HUCRAA (50/50)	A.S.	4	4,8	0,29	40,8	57,7	0,08	4973	1	12 %	23 %	87 %	0,35	-	43	-	67	48,5	-	-	-	-	-	253	-		
	A.S.	4										0,46	-	20	-	39	40	-	-	66	-	-	143	170	-		
	A.S. + 0,2 % CaO	12										0,345	-	57	-	61	59	-	-	-	-	-	263	-			
84.05.25 III	A.S.	3,9	4,1	0,35	39,5	57,8	0,10	5832	1	4 %	13 %	31 %	0,388	-	24	-	45	49,5	-	-	-	-	-	241	-	1,68	
	A.S.	4										0,46	-	12	-	34	39	-	-	34	-	-	128	151	-		
	A.S. + 0,2 % CaO	12,1										0,37	-	37	-	55	59	-	-	-	-	-	267	-	1,68		
84.05.25 IV	A.S.	4	5,7	0,28	39,9	57,1	0,08	6041	2	11 %	22 %	54 %	0,34	-	25	-	68	-	-	-	-	-	-	234	-	1,7	
	A.S.	4										0,45	-	17	-	36	43	-	-	46	-	-	144	167	-		
	A.S. + 0,2 % CaO	12										0,34	-	29	-	53	53	-	-	-	-	-	250	-	1,76		
84.05.25 V	A.S.	4	5,3	0,29	39,4	57,9	0,07	5313	5	14 %	48 %	58 %	0,35	-	35	-	45	47,5	-	-	-	-	-	225	-		
	A.S.	4										0,40	-	25	-	42	44	-	-	75	-	-	156	197	-		
	A.S. + 0,2 % CaO	12										0,35	-	35	-	59	59	-	-	-	-	-	251	-			
84.05.25 I	A.S.		1,3	0,43	39,6	57	0,03	10392	11	56 %	81 %	90 %															
84.05.25 VII	A.S.		0,3	0,38	39,7	57,7	0,04	10872	5	33 %	53 %	93 %															
84.05.25 (I 30 % + V 70 %)	A.S.	4,2											0,42		21		35	35						110	1,67		
	A.S. + 0,2 % CaO	12											0,42				32	30						111	1,6		
84.05.25 (VII 30 % + IV 70 %)	A.S.	4,2											0,41		21		36	36						110	1,6		
	A.S. + 0,2 % CaO	12											0,41		5		47	34						111	1,6		
84.05.25 (I 50 % + II 50 %)	A.S.												0,56		16		22	21			28			50	57		
	A.S.																										
84.05.25 (VII 50 % + V 50 %)	A.S.												0,50		14		21	18			38			51	58		

4.4. Conclusions :

The reliability of the PH. 3. process has been demonstrated during pilot tests. This process allows the production of good quality and high P_2O_5 content acid together with merchant grade calcium sulphate.

By immediately drying the cake from the filter, either hemihydrate or II anhydrite or a mixture of both, are obtained because of their very particular crystallization states. These products exhibits remarkable mechanical properties and this opens new opportunities for new phosphogypsum usages.

Thanks to the pilot tests, it has been possible to define the operating parameters for the treatment of most usual commercial phosphate rocks and the sizing criteria for the various necessary equipments as well as to select the type of equipment.

TA/84/12 Simultaneous production of merchant grade calcium sulphate and high strength phosphoric acid by A. Davister & F. Thirion, Prayon-Rupel, Belgium

DISCUSSION: Rapporteur E. HOLTE, Norsk Hydro, Norway

Q - Mr. J.C. ABRAHAMSE, UKF, Netherlands

Can you give information about cadmium distribution over the acid and calcium sulphate?

A - During the tests we concentrated on making high grade phosphoric acid and calcium sulphate and, although we monitored the impurities in the products, we do not so far have data on the distribution of cadmium.

Q - Mr. K.L. PARKS, Agrico Chemical Company, USA

In table 2 in the paper giving values for the test with Kola/Bu Craa blend you give an increase in the Fe₂O₃/P₂O₅ ratio from the rock of 0.0087 to 0.0108 in the acid. Does this suggest severe corrosion?

A - We utilize stainless steel in our test equipment and the corrosion analysis carried out on the test equipment indicates no corrosion whatsoever.

Q - Mr. R. SMITH, Duetag, France

Could you advise further the uses for the calcium sulphate produced by this process?

A - For upgrading of Ca sulphate, we have already the Central Prayon process. Virtually for all the production of Ca sulphate from that particular process in our own plants, and at the customers' location in Sweden, Japan and Africa, upgrading is done for the production of products which are currently obtained from natural gypsum in the production of β -hemihydrate. If we look into the results, we would find little differences in the quality of β -III-hemihydrate, whether it be phosphogypsum or natural gypsum. We can also use it as cement retarder or as Ca supplier raw material in the manufacture of cement clinker as is done in some countries, like for instance South Africa.

We have developed the PH3 Process because we wanted to have concentrated acid, but we also wanted to retain this possibility of upgrading Ca sulphate. Because of the mechanical properties of the α -hemihydrate, we have found new outlets. Introducing a controlled proportion of II-anhydrite is even more interesting, because II-anhydrite does not need to be produced by high temperature thermal treatment, as is done in plaster works. It is present in the crystals and requires no drying energy. That way we could, of course, replace certain production of plaster by traditional means and also cement in terms of strength and in terms of material design.

Fillers and whatever you might have in mind will be another market.

Q - Mr. K.L. PARKS, Agrico Chemical Company, USA

What results would you expect with Florida 68 BPL rock?

Does this process reduce the radioactivity of the gypsum, i.e. the radium content?

A - We have just completed a test of six weeks on Florida rock. I do not have any electronic microscope presentations and I do not have the results with me, but I can tell you that with the Florida grade 70/72 BPL, we had 46% P2O5 acid obtained with yields of about 99%. The operating factor was just as good as with the Morocco grade and the shape of the crystals was more or less similar, so I can tell you that the grade for the Florida product was easier to achieve than with the Morocco grade, which was pretty good in any case.

During the tests we monitored a certain number of ingredients. Included in these is the monitoring of radium, but the results of these tests are just now under processing.

Q - Mr. J.D. CRERAR, Norsk Hydro Fertilizers Ltd, United Kingdom

The operating conditions given for the 2nd reaction stage are 18-23% P2O5 and for the 3rd stage 24% P2O5. Thus there can be little recovery of P2O5 at the dihydrate separation. How difficult is this operation? Is it by-passed on the pilot plant?

A - What I can say is that the control of the quality of the final Ca sulphate with α -hemihydrate or the mixture of α -hemihydrate and anhydrite II requires essentially that we have a full rehydration in the second phase and this is a must of the process. Separation after the second stage is optional and has nothing to do with the recovery of the characteristics of the products.

Q - Mr. P. MORAILLON, CdF Chimie AZF, France

How can you explain the balance of impurities in the phosphoric acid and Ca sulphate that correspond to it? We altogether find only part of the metal impurities in the phosphate, for instance 32% of Al2O3 in the Kola/Casa grade or 50% Na2O in the Kola/Bu Craa grade according to the figures given in table II.

A - When you have 80% Al2O3 balance when doing experimental work in a pilot plant, it is not that bad. In return, it is pretty obvious that 50% when you do a Na balance is something which is not right. It must be a mistake somewhere. By all accounts, Na in the acid will ultimately be of a slightly higher concentration by the time full equilibrium in the system has been reached.

We have to realize that in a pilot plant, with a 20 kg P2O5/day capacity, there is from a human point of view a maximum you can do. We also have to produce series of samples and samples which in fact require additional purging. At the time of sampling on liquid products at a laboratory level, we can work on the product as

such, but, for reasons of overload, we do it away from the clear liquid. Consequently, we might have precipitation. The sodium might not be present in the liquid phase. That is why you have to do it on the solids rather than on the liquid.

Q - Mr. M. GAURON, COFAZ SA, France

In the Ca sulphate handling section III α -anhydrite seems to be an intermediate between α -hemihydrate and II-anhydrite, but putting yourself in intermediate conditions, you are going to get a mixture of α -hemihydrate and II-anhydrite. How can you account for the absence of the α -hemihydrate III, if put this way?

A - The crystallization phase in the chemistry operations is sophisticated. A lot of literature has been published on this and I think that things are changing pretty fast. So everybody has his own ideas on the issue, and I would say that III-anhydrite is often present. But in doing the analysis and the X-ray diffraction for determination, we cannot make the distinction between α -hemihydrate and III-anhydrite as the spectrums are superimposed on each other. When working out the product, you will have a lot of III-anhydrite present which will activate the setting times.

Q - Mr. P. BAEKEN, Coppée SA, Belgium

On page 2 on the paper, you say that one can resort to silica, which could be added. Could you say more about this? That particular thing is already patented and covered. Please elaborate.

A - Adding silica or the role played by various foreign matters (impurities) present at various levels in the phosphate rocks used, like organics, silica, alumina and many others have been brought forward many years ago. In the beginning of the 60's, recommendations were drafted on the use of these products.

As a matter of fact, later on (some 20 years back) a very interesting paper by Mr. Gilbert, USA, gave a lengthy description of which role is played by a certain number of those impurities or foreign matters and what effect they can have on the crystallization behaviour of Ca sulphate and also on the transition from one form to another. As a matter of fact, as we go along, we get to know how to make the most of the phenomenon and to use it to maximum advantage.

Q - Mr. M. MIYAMOTO, Nissan Chemical Industries, Japan

On figure 3, there is no outlet of filtrate from the dihydrate section. Where does it go?

A - Separation of dihydrate is an operation which is still optional as shown on our flowsheet. But when we incorporate it, that does not necessarily give any outlet because we have the possibility to recycle.

Answers to questions in writing

Q - Mr. J.D. CRERAR, Norsk Hydro Fertilizers Ltd, United Kingdom

The P2O5 recovery of 99-99.5% probably excludes mechanical losses from the filters. With three separation stages this must be significant. Can the authors quantify the overall recovery for an industrial plant?

A - Generally, our design includes one closed circuit for process and cooling waters. In this case, the overall recovery is 99 to 99.5% for an industrial plant. The possible losses will be accidental.

Q - Mr. M. GAURON, COFAZ SA, France

Since phosphoric acid contains less impurities than a dihydrate free acid, the final hemihydrate will be more impure. Please comment.

The phosphates indicated in table II contain little Na. Have you tried phosphates with a higher Na-content? In that case, does the hemihydrate contain more fluorine?

A - No, the final hemihydrate is purer than with a dihydrate process, because impurities are dissolved at this concentration. The impurities are in the product acid.

Yes, we have treated the Casa phosphate rock 68-70 BPL. There is a relation between Na and F content in solids; but values are less than in a dihydrate process.

Q - Mr. M. MIYAMOTO, Nissan Chemical Industries, Japan

How do you positively proportioned α -hemihydrate and II-anhydrite in dihydrate hemihydrate conversion stage, by temperature or by H2SO4 concentration therein?

Is it possible to make II-anhydrite free of hemihydrate?

What is the allocation of 98% H2SO4 into the three stages?

A - The concentration of II-anhydrite in hemihydrate and dihydrate conversion stage is controlled by adjusting temperature, P2O5 and H2SO4 concentration in the liquid.

In the wet phosphoric acid processes II-anhydrite is made from hemihydrate and dihydrate conversion. There are some free II-anhydrite crystals in the produced solids.

The distribution of sulfuric acid introduced in the three phases of the process is about:

- hemihydrate attack section	50%	25%
- dihydrate conversion section	25%	25%
- hemihydrate conversion section	25%	-
- II anhydrite conversion section	-	50%

Q - Mr. M. BARLOY, Office Togolais des Phosphates, Togo

Does the first hemihydrate reactor include several compartments?

Does the process described have an economic advantage if the calcium sulfate is not processed? In particular, can you eliminate the third stage?

A - The multicompartimented single tank coupled with the new low level flash cooler organized to ensure separate control on the three flows (through the tank, through the flash cooler and inside each compartment) as well as to minimize the power rating by the use of helicoidal pumps and carefully shaped agitators has now reached full maturity and strength. It is of course one of the main topics of the hemihydrate reaction together with the digestion tank(s) in which the slurry is adjusted and stabilized before filtration.

If the gypsum is not processed, the third stage is of no interest except in case of dry handling to disposal, which is more easily achieved when the process delivers a self drying mixture of α hemihydrate and II-anhydrite. But of course who can do the most can do the least and as a fall out of the PH3 process we have developed a full range of hemihydrate processes named PH for Prayon hemihydrate. These are either straight hemihydrate in one stage (PH11) or in two stages (PH12), or hemidihydrate in two stages (PH2).

Q - Mr. N.D. WARD, Norsk Hydro Fertilizers Ltd, United Kingdom

Results are given only for the rock mixtures including Kola-apatite. How does the plant perform on a sedimentary rock alone?

A - During the lecture, we have shown results obtained with commercial Kouribga rocks and indicated figures obtained during a run with commercial Florida rock. Both behaved perfectly well. If our tests were started with Kola apatite containing rock mixtures, this is simply to adapt it to our usual plant feedstock.

Q - Mr. T.J. THOONEN, UKF, Netherlands

Can you give figures in p-Curies/g over the different steps (HH-DH-HH)?

A - Without special treatment the radioactivity is the same over the different stages.

Q - Mr. N. TURKI, SIAPE, Tunisia

Do you add chemicals to prevent formation of dihydrates in the first crystallization?

A - No, but it is necessary to adjust the conditions for hemihydrate crystallization.

