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- Its latest improvements with various phosphate rocks.
- Its applications to the revamping of industrial units through the experiences of SICNG (GREECE), RHONE POULENC RIEME (BELGIUM), ICS (SENEGAL)

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SUMMARY

This publication presents the latest development in the RHONE-POULENC DIPLO patented process for phosphoric acid production.

The research in raw materials and energy saving, the adaptation to new ore quality and the desire for reliability improvement its industrial units as well, have led RHONE POULENC to optimise its process.

This is why new investigations have been started on a laboratory scale in order to point out the compared advantages between the single tank and the DIPLO process.

The exploitation of 5 phosphoric acid production units of which 3 out of them have been recently revamped according to the DIPLO process allows RHONE POULENC to compare conclusively its research results with its industrial practice.

1 - INTRODUCTION

Most producers of phosphoric acid today use the dihydrate process for the obvious reasons of simplicity and reliability. It is in this spirit that RHONE-POULENC, which currently has 5 production sites, wishes to develop its process which consists of the following steps :

- the attack of phosphate rock in a non compartmented air cooled reactor with one central agitator and a very simple air scrubbing system (1,2).

- the gypsum filtration on a flat rotating table : the UCEGO filter worldwide known for its easy operation (3).

- the concentration in a single stage evaporator using a forced circulation loop with recovery of fluosilicic acid.

This process has been studied and improved for many years and one may think that the maturity level has been reached. Nevertheless, RHONE-POULENC notes the following :

- as a producer, RHONE-POULENC is aware that profits generated by each innovation and improvement in technology, however small, are significant.

- as a buyer of phosphate, RHONE-POULENC must always be adapting to new sources of materials.

- as a licensing company, RHONE-POULENC is obliged to find a solution for each client which meets their specific needs.

This is why the laboratory of the **Techniques and Processes"** center is pursuing an intensive research programme in which more than 1200 of phosphoric attack tests on more than 200 different phosphate rocks have been undertaken.

It is also at the center that the DIPLO process, which is the subject of this communication, was developed and commercialised.

2 - PRINCIPLE OF THE DIPLO PROCESS

The DIPLO process has been developed step by step over the last 10 years. It has already been described in 1979 (4),1984 (5) and 1987 (6).

The basic principle is the following : with the attack of phosphate rock by sulfuric acid one must optimize three interacting criteria :

- the dissolving of phosphate : which determines the yield and the size of the reactor.
- the filtration of the slurry : which determines the washing efficiency and the size of the filter.
- the concentration of P2O5 : which determines the steam requirement and the size of the concentrator.

In a single tank a compromize must be found between these three criteria in one step.

We therefore place ourselves most often :

- with a maximum excess of sulfate (20 - 40 g/l depending on the phosphate) against the risk of attack blocking and a reasonable consumption of sulfuric acid.
- with a maximum concentration of P2O5 (26 - 30% depending of the phosphate) compatible with a good filtration.

The concentration of free sulfate, which is beneficial to the yield (drop of co-crystallized P2O5 losses), combined with a high concentration of P2O5 can cause the start of hemihydrate production and all of its bad consequences.

In the DIPLO process one feeds the phosphate and sulfuric acid into two tanks in series, thereby optimizing the three criteria separately :

- in the first tank one optimizes the yield and the filtration rate by maintaining a high concentration of free sulfate and a low P2O5 concentration : in this way one starts a good crystallization and minimizes co-crystallized losses.
- in the second tank by addition of phosphate and sulfuric acid one adjusts the concentration of free sulfate to a minimum and raises the P2O5 concentration to a maximum.

This two stage attack therefore permits :

- an improvement in yield for 3 reasons

  . less co-crystallized P205 losses
  . less unattacked P205 losses by a better residence time distribution
  . less water soluble losses at the filtration level by a better crystallization

- a better filtration rate for same P205 concentration

- a higher operating easiness due to crystallization conditions in the first tank further of hemihydrate area.

This is what we call the DIPLO effect

The extent of this effect depends directly on :

- the gap of concentration between the 2 tanks
- the gap of concentration of free sulfate between the 2 tanks.

These gaps are a function of :

- the nature of the phosphate rock (origin and composition) (figure 1)
- the nature of feed rock (dry rather than wet) (figure 2)
- the granulometric distribution (grinding or not)
- the concentration of sulfuric acid
- the phosphate repartition between the 2 tanks (figure 3)

These influences have already been shown (6) and one should remember that under the following conditions the best DIPLO effect is obtained :

- phosphate with the lowest retention rate of solution in the gypsum
- the dry feed rock rather than wet feed rock
- the highest concentration of sulfuric acid (98%)
- to feed tank 1 with 50 to 80% of the total phosphate
- a weak granulometric phosphate size.

Previous laboratory results on various phosphates will be presented first. Then actual industrial performances obtained with RHONE-POULENC's units in particular :

- results obtained recently at SICNG
- results obtained at the RIEME plant which came on line in 1989
- option selected and results expected in the revamping of phosphoric unit in SENEGAL (ICS) today in progress.

Finally this report will finish with an economic and technical study comparing the single tank and DIPLO processes.

3 - PERFORMANCES MEASURED WITH SEVERAL PHOSPHATE ROCKS - COMPARISON WITH SINGLE TANK PROCESS

- Many laboratory tests have been performed lately to demonstrate the advantages of the DIPLO process on single tank process and to chart its limits.

- With four reference phosphate rocks we drew experimental graphs to evaluate the influence of different parameters in these two processes.

3.1. Phosphate rock selected

A. Phosphate rock from TAIBA

Sedimentary rock with clayey gangue, TAIBA is a phosphate rock showing a good crystallization behaviour and therefore a good filtration.

Main characteristics

Specific surface BET (quite good)	: 10 m2/g
CO_2 content	: 1.2 to 1.5%
Al_2O_3-Fe_2O_3	: 2%

B. Phosphate rock from KHOURIBGA

Sedimentary rock with carbonated gangue, KHOURIBGA is one of the famous Morocco rock most often used in the world.

Main characteristics

Specific surface BET (important)	: 17 to 20 m2/g
CO_2 content	: 5 to 6%
Al_2O_3-Fe_2O_3	: 1%

C. Phosphate rock from YUNNAN (ANNING Mine)

Sedimentary rock with siliceous gangue, YUNNAN is one of CHINA's phosphates.

Main characteristics

Specific surface BET	: 10 m2/g (same as TAIBA)
CO_2 content	: 2 à 3%
Al_2O_3-Fe_2O_3	: 2%

Let us note the evolutionary character of this phosphate about MgO content (0,13% today ; more than 1% several years ago).

D. Phosphate rock from SOUTH AFRICA : PALFOS

Typical igneous rock, the PALFOS is richer in P_2O_5 but less porous, and so needs more time for digestion.

Main characteristics

Specific surface BET	: 0.4 to 0.5 m2/g
High P_2O_5 content	: 38%
No organic carbon	
Al_2O_3-Fe_2O_3	: 0.2 to 0.3%

3.2. Comparison criteria

Criteria selected are following :

- the concentration of filtered phosphoric acid : % P2O5 in the acid product.
- the attack P2O5 yield : ratio P2O5 in the acid/P2O5 in the phosphate

  Note : the laboratory washing efficiency always more than 99.5% is not included.

- specific volume : useful tank volume/metric ton per day P2O5 produced.
- filtration rate : : MTPD P2O5 produced/square meter of filter under vacuum.

  Note : this filtration rate coming from lab test on static filter is translated in industrial values with following assumptions :

Rotating speed of the filter	: 0,5 rpm
Number of counter current washes	: 2
Gypsum removal	: wet form

3.3. Results

You will find figures (4) to (7) results achieved with selected phosphate rocks illustrated by 4 network curves :

Curve a : variation of attack yield versus acid concentration
Curve b : variation of the filtration rate versus acid concentration
Curve c : variation of attack yield versus specific volume at constant P2O5 concentration of the product acid
Curve d : variation of the filtration rate versus specific volume at constant P2O5 concentration of the product acid.

These curves, being a kind of identity card of these phosphate rocks, show us :

1. Decrease of yield when the concentration of product acid increases : with the decrease about 0,4% to 1% (depending of the phophate rock) the concentration of the product acid increases from 26 to 30%

2. The gain of attack yield with the specific volume : this well known result depends of the reactivity of the phosphate rock.

3. The decrease of filtration rate with the P2O5 concentration of the product acid.

4. The slight variation of filtration rate with the specific volume.

DIPLO effect appears at two levels :

- Increase of **attack yield** : it is clearly in evidence for all phosphate rock and varies from 0.3 to 0.5% when one goes from a single tank to DIPLO process, all other things being equal.

- Increase of **filtration rate**, it is highly variable depending on the phosphate rock :

  * 25% for YUNNAN
  * 10% for KHOURIBGA
  * 5% for the PALFOS
  * 3% for TAIBA

This increase, due to an improvement of the gypsum crystallization, is not predictable by the type of phosphate at the current level of knowledge : all attempts of correlation using composition of physical characteristics of phosphate rocks were in vain. Therefore we are still dependent on laboratory tests despite the extensive data that has been accumulated.

4 - INDUSTRIAL EXPERIENCES

4.1. SICNG - GREECE

The revamping of the unit made in 1982 has already been described in previous publications.

The plant with a capacity of production of 250 MTPD (P205 concentration 28/29%) was fitted out with 2 reactors (300 + 200 m3) and 2 tilting pan filters of useful area 18 m2 each.

The existence of two reactors and the wish of operators to change the two filters with only one, brought RHONE-POULENC to suggest the revamping of the plant in accordance with the DIPLO process.

Three modifications were carried out :

- the taking over from two existing filters, with one UCEGO filter n° 7 (63 m2 of usefull area).

- the fitting up of raw material feeding (rock and sulfuric acid) and recycled phosphoric acid to allow the running in series of the two reactors.

- the taking over of scrubbing system of gas from reactors, with a new one made up of a venturi and a cyclonic column in series.

Realised performances

- Figure 8 shows the results obtained for the new capacity of 360 t/d.
  One of the main advantages of the process is the great flexibility of the modified plant : phosphates as different as TAIBA, TOGO, JORDAN, MOROCCO KHOURIBGA, DJEBEL-ONK have been used with only a few alterations in the performance of the plant.

- In spite of the increase in production rate due to the replacement of the filters, we obtained a yield gain due to the DIPLO process of 0,5%, through a decrease of the co-crystallized loss.

- The P205 concentration of product acid, was maintained between 28 and 29%, whatever phosphate rock was fed.

Recently, some modifications of running parameters of the plant have been carried out, in order to increase the P205 concentration of product acid.

The phosphate repartition between the two reactors has been specially modified to increase the P205 concentration. In this way, with TAIBA rock, a P205 concentration of 32% to 33% has been reached in industrial running, but with a slight decrease of the washing efficiency due to the increase of water soluble losses. The total efficiency was 95,7%. It would be possible to reduce these losses, by addition of a third washing on the filter.

4.2. ICS : SENEGAL

- The unit has been designed in 1984 for a capacity of 720 MPD, with a feeding of a mixture of TAIBA phosphate rock and Schlamms. The expected capacity after modifications will reach 1015 MTPD.
  Actually the plant is fitted out with one single reactor, and two filters (UCEGO 10 and UCEGO 7) operating in parallel.

- Based on pilot tests with the mixture, the choice alternatives were the following :

Equipments	2 lines in parallel 1 single reactor (existing) 1 filter U10 (existing) 1 reactor (new) 1 filter U7 (reused)	2 reactors 900 m3 in series (1 existing) (1 new) 2 filters in parallel (existing)
Specific volume (m3/t P205/24h)	1.6	1.6
Concentration of the product acid (% P205)	28.8	29.6
Attack-filtration yield (%)	96	96,3
Capacity of filtration (MTPD of P205/m2 useful area	6.1	6.1

The choice of the DIPLO process has been made by reason of :

- increase of the yield (+ 0,3%)
- increase of the concentration of acid (+ 0,8%)
- easier operating conditions

Planned modifications

- Construction of new reactor of 900 m3, with its scrubbing system for waste gases.
- Retrofitting out of evaporator lines in order to concentrate the additional capacity.

4.3. Attack of RIEME plant, revamping

Introduction

The factory of RIEME was operating a phosphoric acid unit started up in 1957, in accordance with a very old KUHLMANN process. In 1983, the unit became subsidiary of RHONE POULENC and has been the subject of several revampings.

- In 1987 the DORR OLIVER filters of 16 m2 each, that is, 64 m2 total area, has been taken over with only one UCEGO filter n° 8 of 85 m2 useful area.

  This investment allowed to increase the total yield, on average of 1.7 point and the concentration of product acid to 0,75 point with decreasing of maintenance costs.

- In 1989, RHONE-POULENC, decided to change the attack system, as described here after.

Choice of attack process

The previous attack system, with a total capacity of 130000 MTPY, was fitted out with two lines in parallel, each with two reactors in series. The two lines were connected with a single feed tank.
The total attack volume was : 420 m3 in 5 tanks, with the performances as following :

Rock	Jordan	Palfos
Industrial yield	91%	93%
Acid concentration % P205	26,5	27

To take over this attack system, 2 options have been studied :

- a single tank of 700 m3.
- the DIPLO process with 2 reactors of 350 m3.

Some pilot tests were made with a mixture of 80% Palphos and 20% Jordan and gave the following results

		DIPLO/single tank
Co-crystallized losses	%	- 0,25
Unattacked losses	%	- 0,05
Water soluble losses	%	- 0,2
Total yield	%	+ 0,5
P205 concentration	%	+ 0,9

The estimated overcost of investment for the DIPLO process was 3.5 MF (on a total investment of 30 MF, for the revamping of attack system).

The pay back calculated, from the improvements of yield and concentration has been evaluated at 13,4 months.
Thus DIPLO process has been selected (figure 9).

Actual running

The new unit started up in June 1989. The mean industrial performances are as follows :

Rocks		Jordan	Palphos
Washing yield	%	98,9	99,4
Total yield	%	95,5	97,1
Concentration	% P205	28,6	30

We point out 2 observations of this unit :

- by using pumps with low NPSH, the level of the filter is low enough to receive by overflow the slurry from the second reactor of the DIPLO. So one saves a phosphoric acid slurry pump and an additional tank.

- the revamped unit includes a centralized system where all data of the unit are collected. This system is connected with a calculator to which an expert system is set up.
  Thanks to this system, the operator can get all information at once. He can run the unit by anticipating events rather than correction of a problem, which is a considerable progress.

5 - ECONOMICAL COMPARISON BETWEEN SINGLE TANK AND DIPLO PROCESSES

The comparison concerns the two processes single tank and DIPLO according to the following assumption : capacity of 700 Mt/day as 54% P205 phosphoric unit, using a phosphate rock with 34% P205 and a good fineness (particle sizes less than 400 microns) leading to average performances with DIPLO process.

5.1. Process and design assumptions

One admitted that with the selected phosphate rock the performances obtained in pilot are the following :

	Single tank	DIPLO	Gap
Attack yield	96.2	96.5	0.3%
Concentration	29%	30%	1%
Filtration rate (t P205/d/m2)	5.2	5.2	0

The following data gives the main equipment specifications according to both processes :

Capacity 700 Mt P205/day		"single reactor"	"DIPLO"
- Reactor(s)	Number	1	2
	Volume(s)	1100 m3	550 m3 + 550 m3
- Agitator (reactor) Number		1	1 + 1
- Reactor (s) scrubbing system (to reach EPA standard for F- effluent)		1 scrubbing system with 4 absorption stages	1 single scrubbing system (4 stages) for the two reactors
- Filtration		1 UCEGO filter n° 11 (useful area 135 m2)	1 UCEGO filter n° 11
- Clarification unit of the diluted acid		1 unit	1 unit
- P205 content in the diluted acid		29%	30%
- Concentration unit up to 54% P205 including the fluorine absorption section (H2SiF6 production)		2 parallel lines with the total evaporation capacity of 44.56 t/h	2 parallel lines with a total evaporation capacity of 41.36 t/h

5.2. Investments costs (indicatives values)

These investment costs (ISBL) excluding the grinding are summarized by section in the following table :

Investments in million US $ and French Francs FF	"Single reactor"	"DIPLO"
1. Section Attack + filtration + acid clarification + diluted acid storages	95 MFF ou (15.83 M$)	98.8 MFF ou (16.46 M$)
2. Section Reactor(s) scrubbing system	13.00 MFF or (2.17 M$)	13.4 MFF or (2.24 M$)
3. Section Concentration	25.5 MFF ou (4.25 M$)	24.5 MFF ou (4.08 M$)
Total cost of the P2O5 unit	133.5 MFF ou (22.25 M$)	136.7 MFF ou (22.78 M$)
Difference of investment cost between "DIPLO" and single reactor"	-	+ 3.2 MFF (+ 0.53 M$)

Thus the difference of investment cost between "DIPLO" and "single reactor" is + 2.4%.

5.3. Gap on manufacturing costs

The raw material and utilities consumptions are estimated as follows :

Per 1 ton of produced P2O5 as 54% P2O5	"Single reactor"	"DIPLO"
- Dry phosphate rock consumption (t)	3.057 t	3.047 t
- Sulfur consumption (t)	0.866 t	0.863 t
- Power consumption (kwh)	72 kwh	73 kwh
- Steam consumption (t)	1.88 t	1.75 t

The variable costs are calculated according to the following basis :

Phosphate rock : 60 $/t (according to the plant site)
Sulfur : 110 $/t
Power : 0.07 $/kwh
Steam : 10 $/t

Variable costs in US dollars $ or French Francs FF per 1 ton produced P205	"Single reactor"	"DIPLO"
	(Basis 1 US $ = 6 FF)	
- Dry phosphate rock - Sulfur - Power - Steam LP	183.42 95.26 5.04 18.80	182.82 94.93 5.11 17.50
Saving (DIPLO compared to the single reactor) Annual saving (basis 7500h/y) for 218000 Mt P205/year Soit 218000 Mt P205/an	- -	2.16 $/t P205 0.470 M$ ou 2.82 MFF (M = Million)

5.4. <u>Selected process</u>

With the performances of the selected standard phosphate rock we see that investment overcost of the DIPLO process compared to the "single reactor process" is paid in about 1.2 year.
RHONE POULENC realise the same economical and technical comparison for each project taking the performances of the used phosphate rock and the freight into account to adjust the comparison with the used phosphate rock and transport costs.

CONCLUSION

This study allows us to show the influence of the selected criteria for the choice of the attack process for new and revamped units.

We have insisted on the necessity to determine the behaviour of each phosphate in pilot scale since knowledge of ore chemico-physical features do not allow the selection of the best process.

The process choice is carried out from the economics of investment and production costs based on these pilot tests.

In fact, for the majority of the cases studied by RHONE POULENC in the last few years, the techno-economic optimisation has led to the choice of the DIPLO process.

It has been the case for the industrial sites of RP (SICNG, DONAU CHEMIE and RIEME) and for licensees as well (ICS).

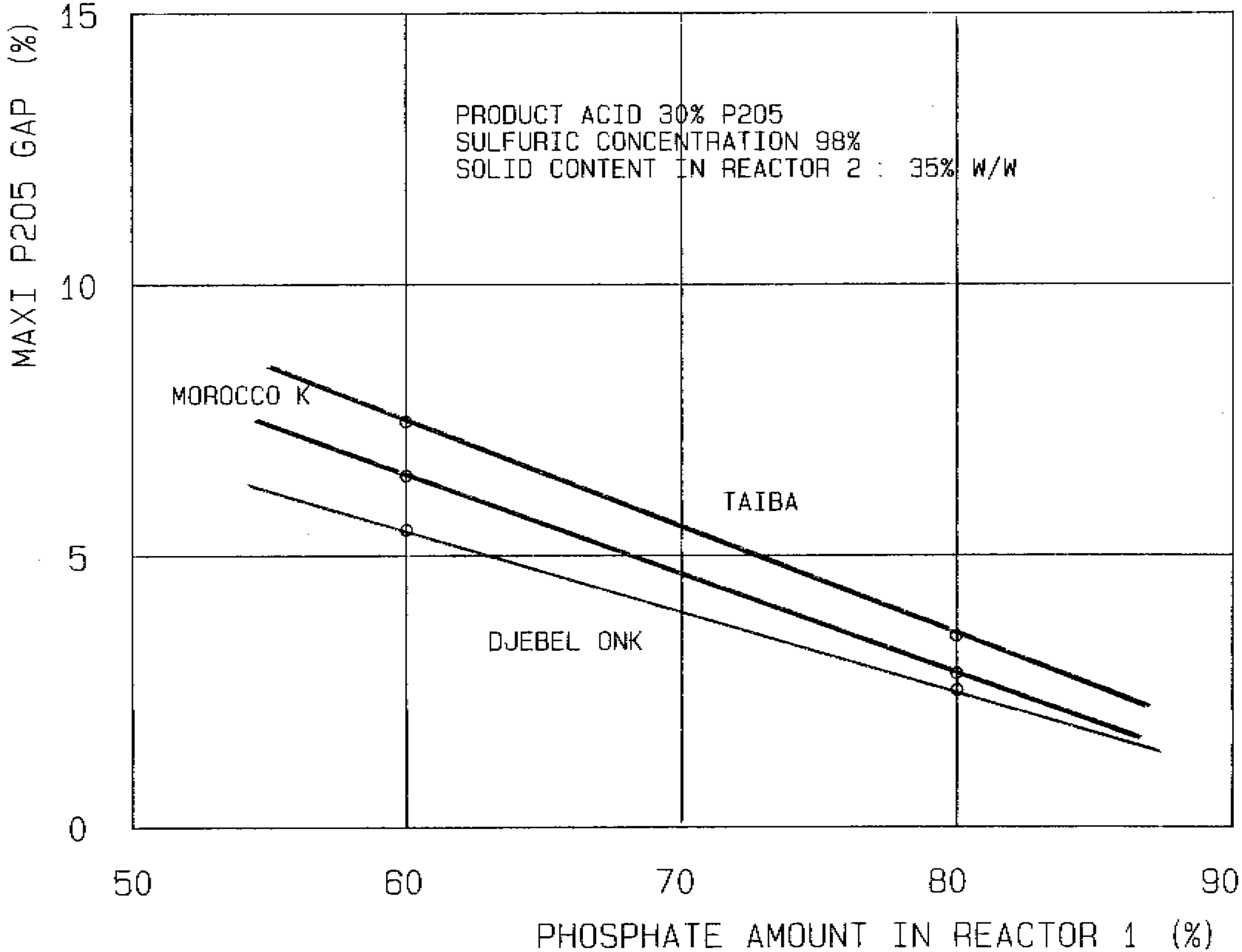
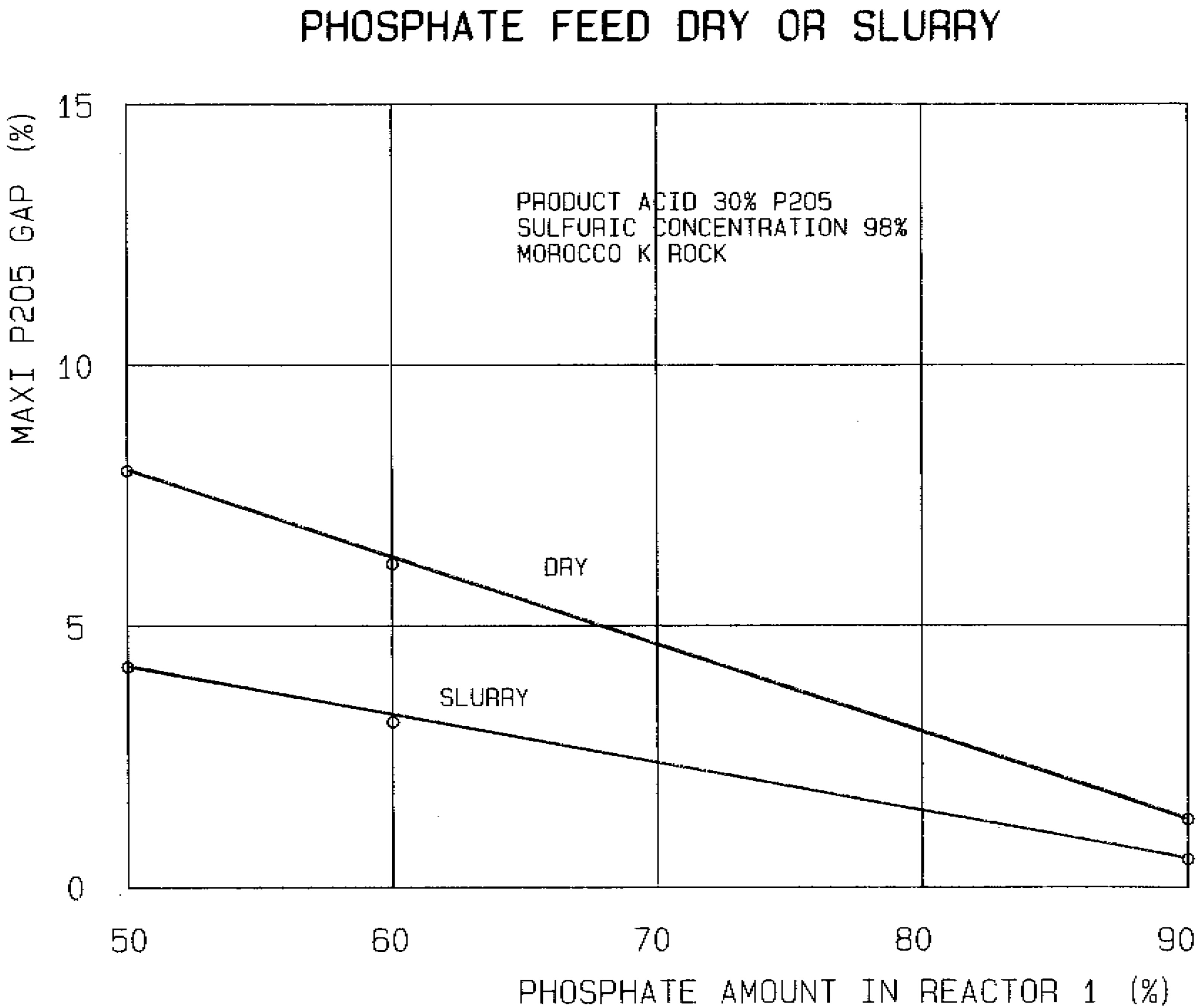

PRODUCT ACID 30% P205
SULFURIC CONCENTRATION 98%
SOLID CONTENT IN REACTOR 2 : 35% W/W
MOROCCO K
TAIBA
DJEBEL ONK
MAXI P205 GAP (%)
15
10
5
0
50
60
70
80
90
PHOSPHATE AMOUNT IN REACTOR 1 (%)

FIGURE 1



17 - 13

FIGURE 2

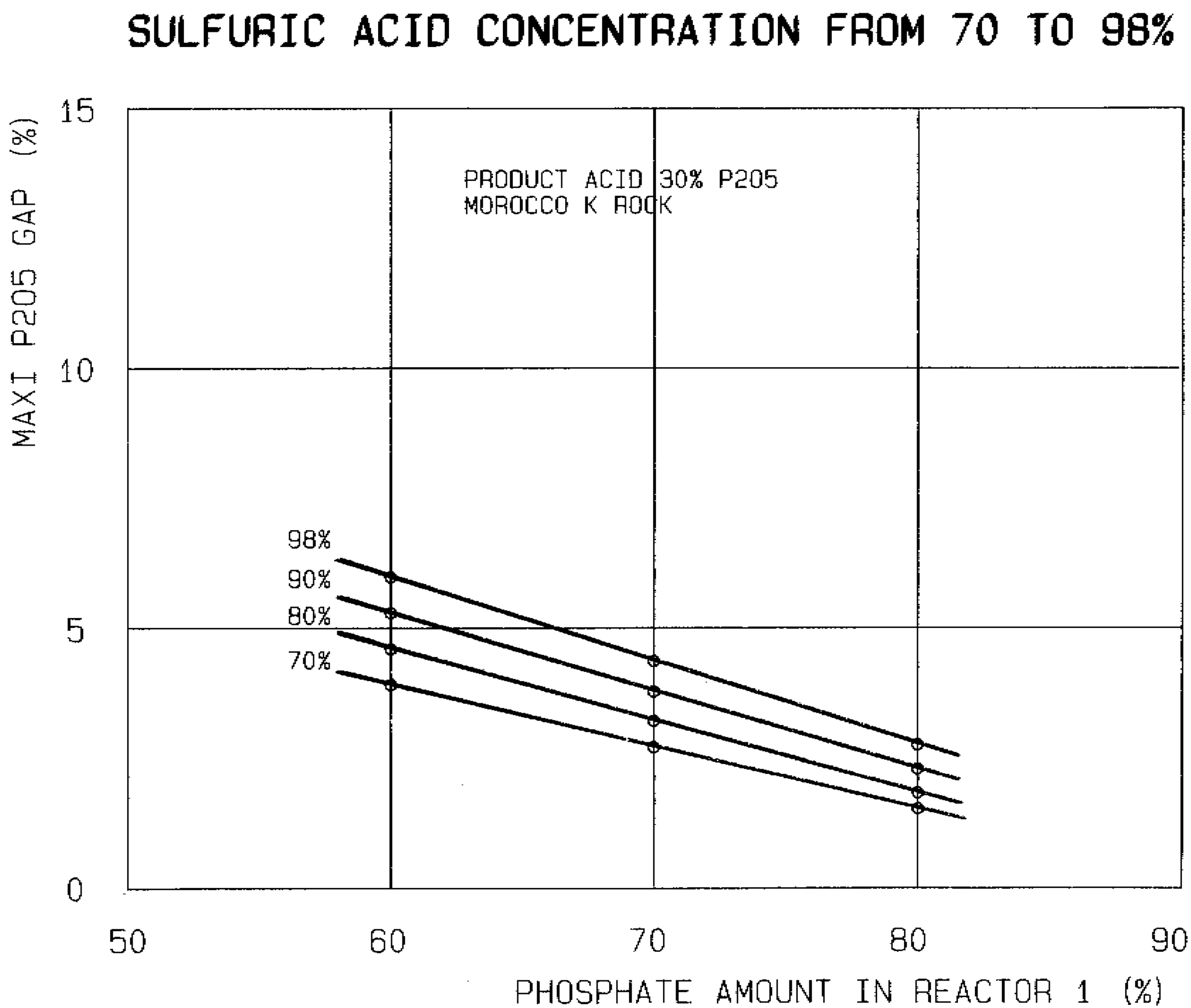
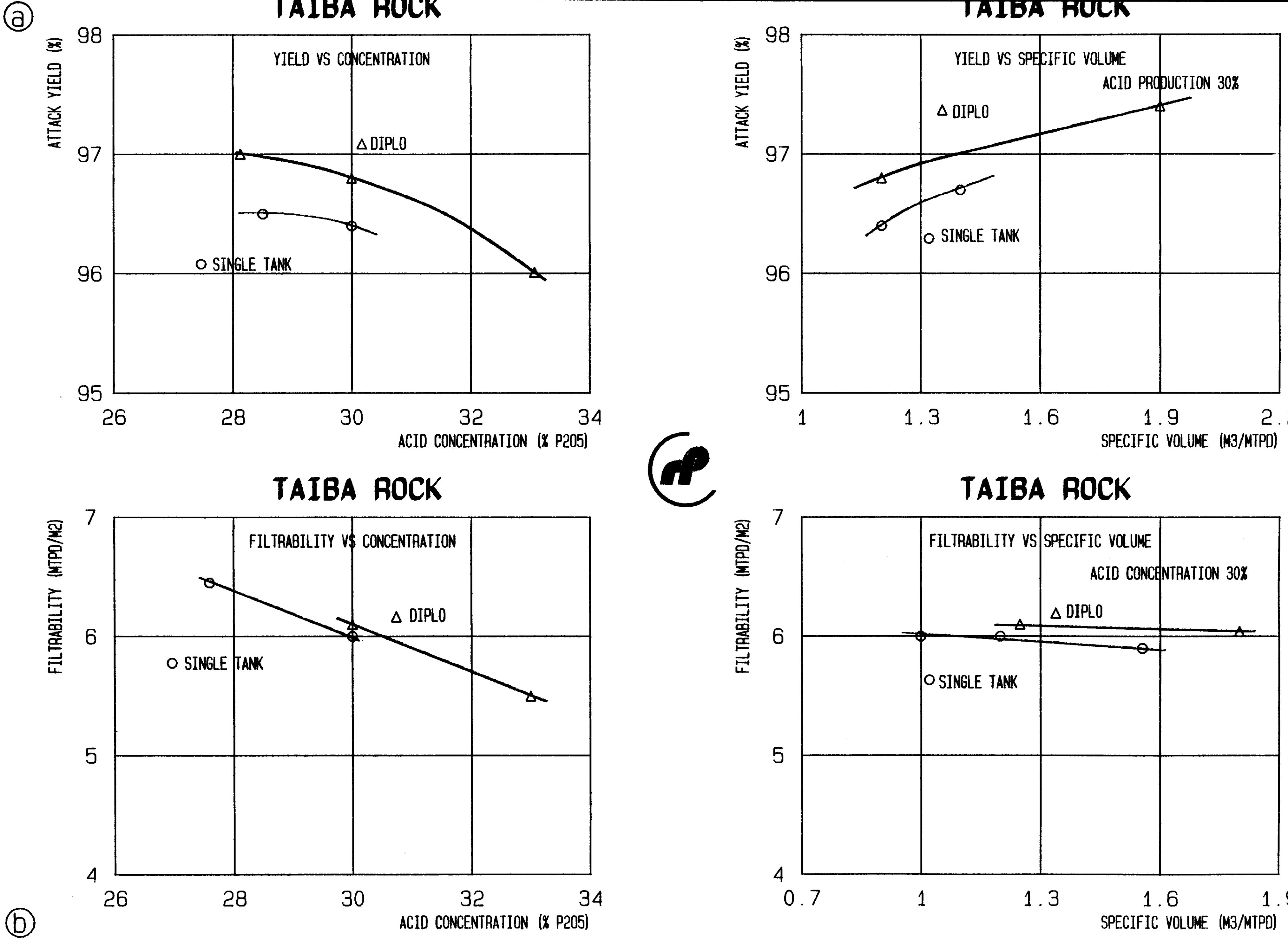
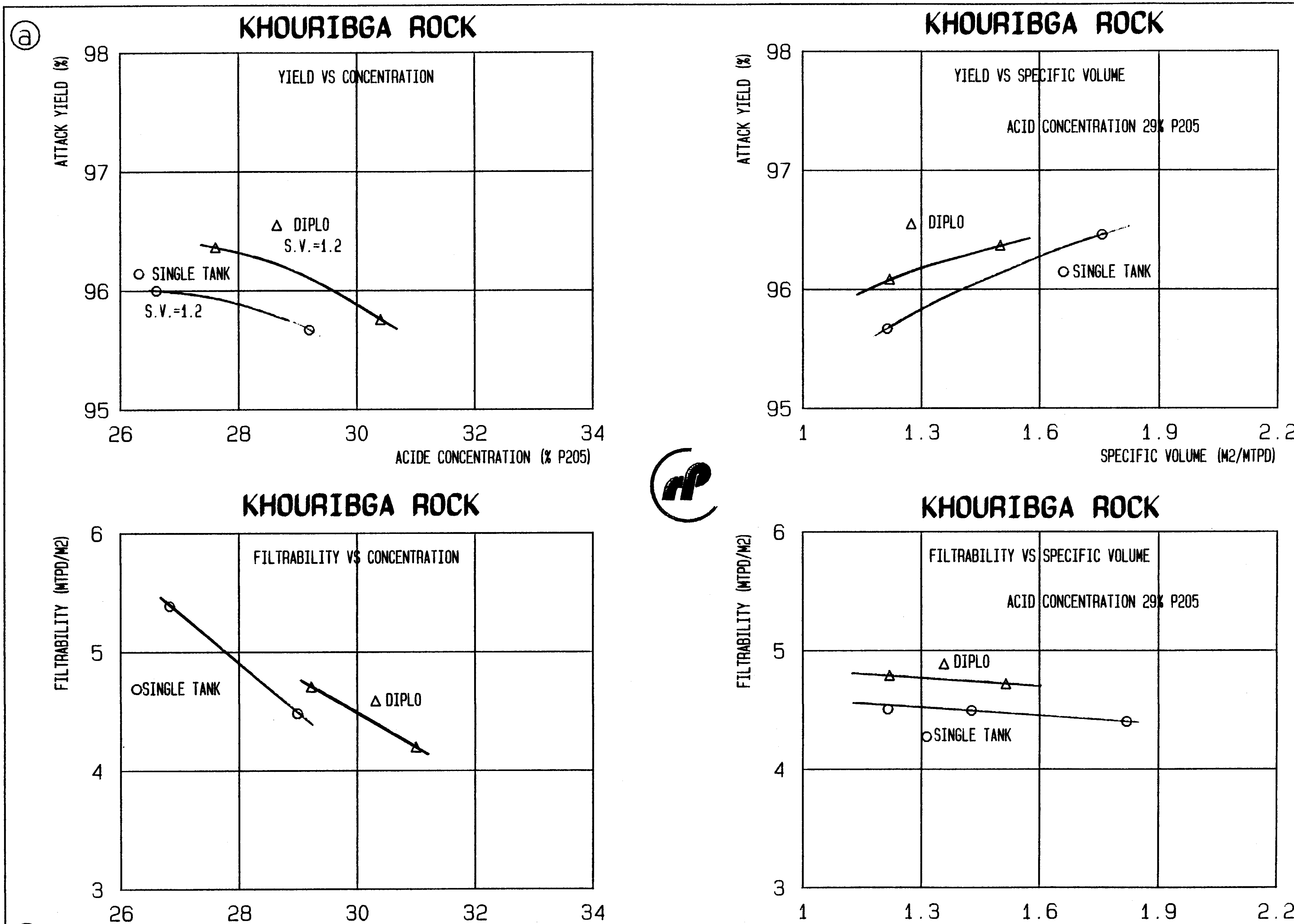

SULFURIC ACID CONCENTRATION FROM 70 TO 98%
PRODUCT ACID 30% P205
MOROCCO K ROCK
98%
90%
80%
70%
MAXI P205 GAP (%)
15
10
5
0
50
60
70
80
90
PHOSPHATE AMOUNT IN REACTOR 1 (%)

FIGURE 3



ⓐ
TAIBA ROCK
YIELD VS CONCENTRATION
ATTACK YIELD (%)
ACID CONCENTRATION (% P2O5)
DIPLO
SINGLE TANK
98
97
96
95
26
28
30
32
34
ⓒ
TAIBA ROCK
YIELD VS SPECIFIC VOLUME
ACID PRODUCTION 30%
ATTACK YIELD (%)
SPECIFIC VOLUME (M3/MTPD)
DIPLO
SINGLE TANK
98
97
96
95
1
1.3
1.6
1.9
2.2
ⓑ
TAIBA ROCK
FILTRABILITY VS CONCENTRATION
FILTRABILITY (MTPD/M2)
ACID CONCENTRATION (% P2O5)
DIPLO
SINGLE TANK
7
6
5
4
26
28
30
32
34
ⓓ
TAIBA ROCK
FILTRABILITY VS SPECIFIC VOLUME
ACID CONCENTRATION 30%
FILTRABILITY (MTPD/M2)
SPECIFIC VOLUME (M3/MTPD)
DIPLO
SINGLE TANK
7
6
5
4
0.7
1
1.3
1.6
1.9

FIGURE 4



17 - 16

FIGURE 5

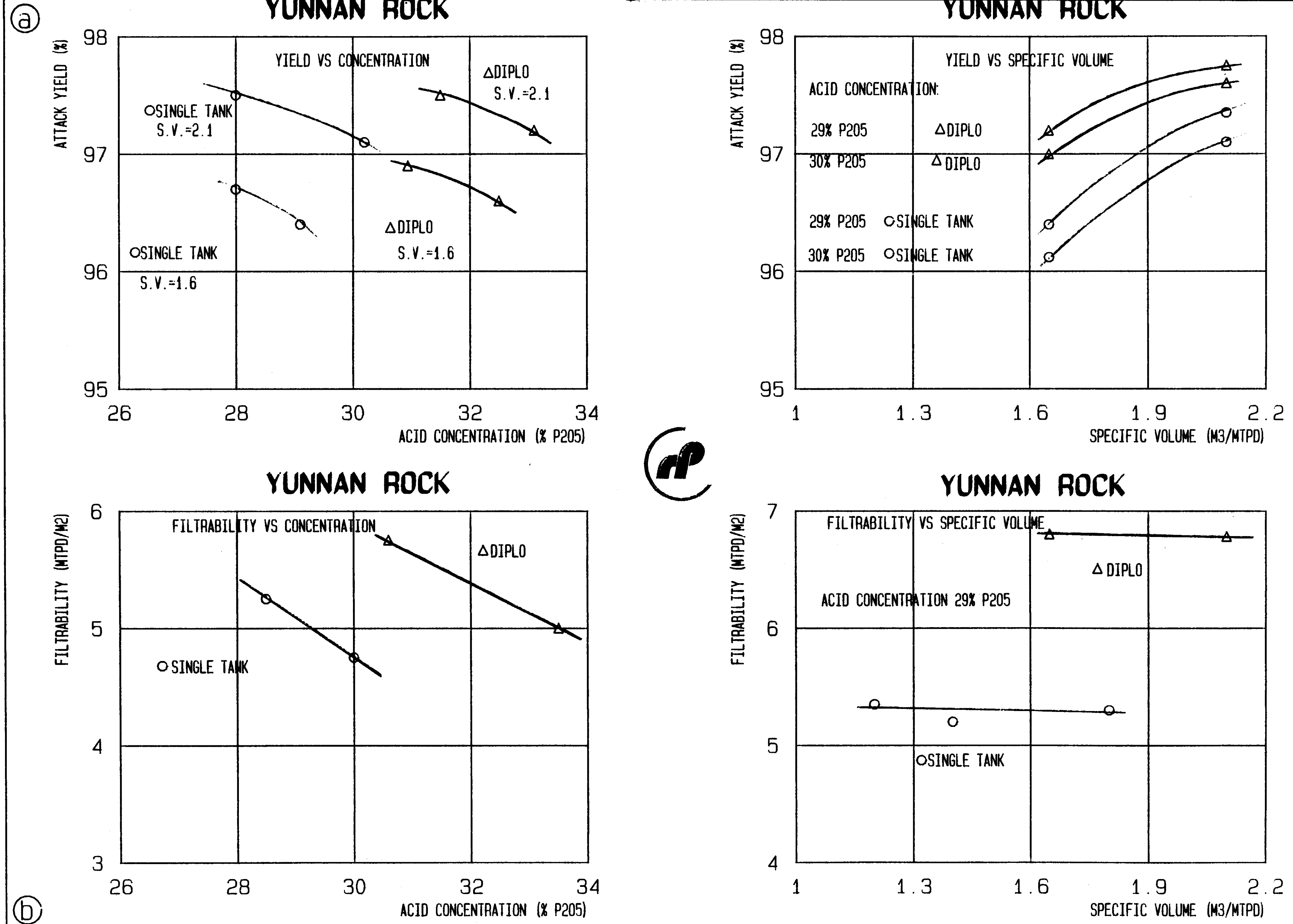

a
YUNNAN ROCK
YIELD VS CONCENTRATION
ATTACK YIELD (%)
98
97
96
95
○SINGLE TANK
S.V.=2.1
△DIPLO
S.V.=2.1
○SINGLE TANK
S.V.=1.6
△DIPLO
S.V.=1.6
26
28
30
32
34
ACID CONCENTRATION (% P205)
c
YUNNAN ROCK
YIELD VS SPECIFIC VOLUME
ATTACK YIELD (%)
ACID CONCENTRATION:
29% P205
△DIPLO
30% P205
△DIPLO
29% P205
○SINGLE TANK
30% P205
○SINGLE TANK
1
1.3
1.6
1.9
2.2
SPECIFIC VOLUME (M3/MTPD)
b
YUNNAN ROCK
FILTRABILITY VS CONCENTRATION
FILTRABILITY (MTPD/M2)
6
5
4
3
△DIPLO
○SINGLE TANK
26
28
30
32
34
ACID CONCENTRATION (% P205)
d
YUNNAN ROCK
FILTRABILITY VS SPECIFIC VOLUME
FILTRABILITY (MTPD/M2)
7
6
5
4
△DIPLO
ACID CONCENTRATION 29% P205
○SINGLE TANK
1
1.3
1.6
1.9
2.2
SPECIFIC VOLUME (M3/MTPD)

FIGURE 6

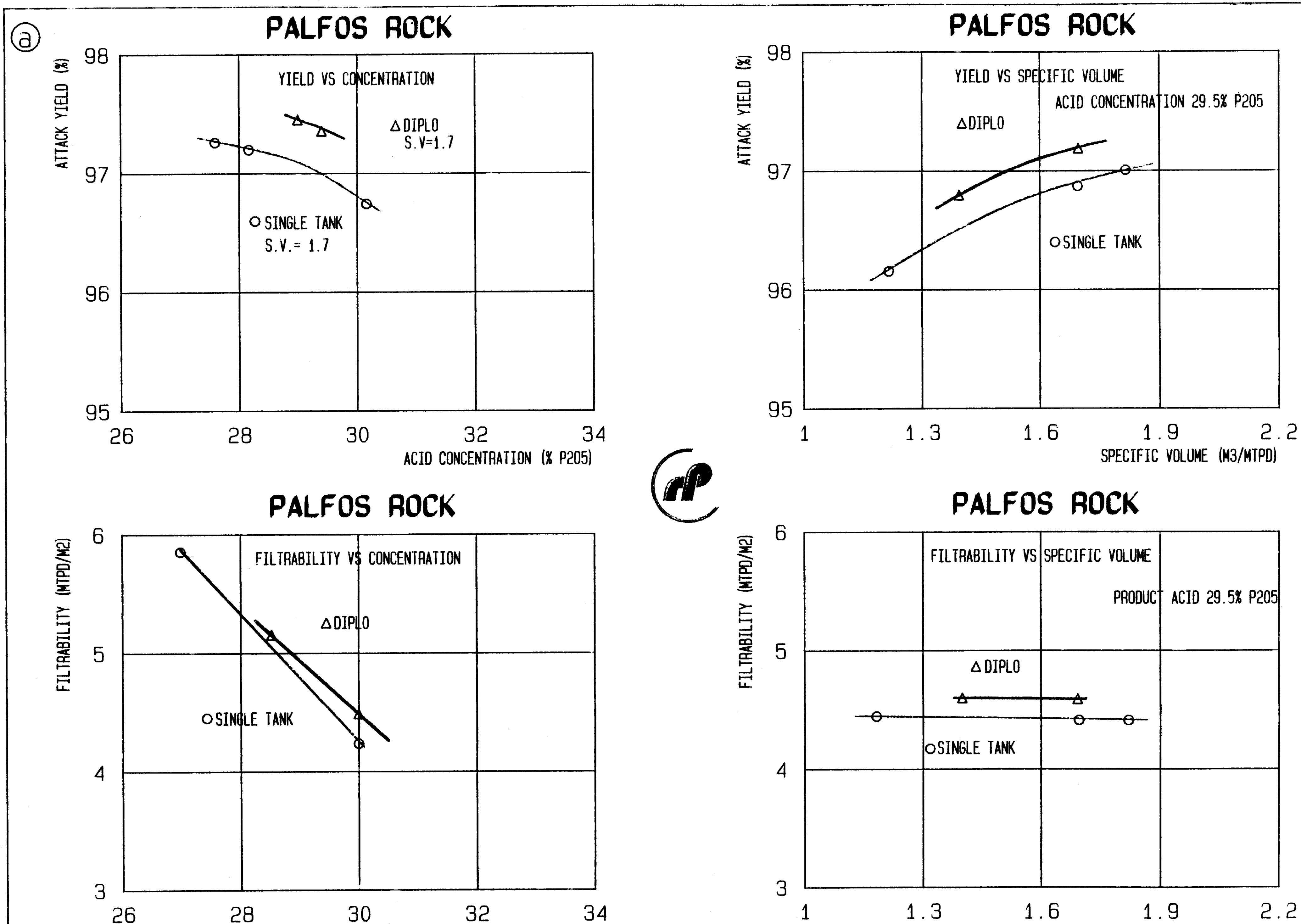


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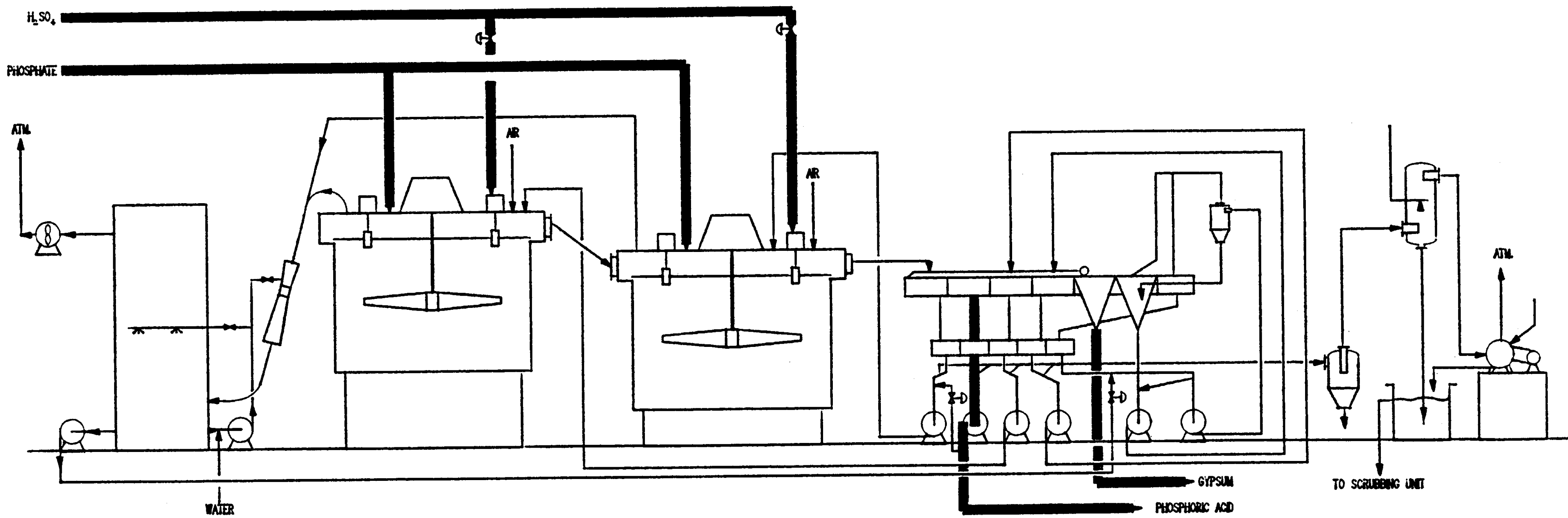
FIGURE 7

FIGURE 8

SICNG THESSALONIQUE (GREECE)

	TAIBA	KHOURIBGA + TAIBA	TOGO	BUCRAA + TAIBA
Grinding %< 80 microns	30	21	12	35
Specific volume (m3/MTPD)	1.4	1.5	1.4	1.4
Repartition phosphate				
Tank 1	70	68	67	70
Tank 2	30	32	33	30
Free sulfate in :				
Tank 1 (g/l)	45	55	50	40
Tank 2 (g/l)	25	25	25	25
Concentration P2O5				
Tank 1	25.5	24.5	25.5	25
Tank 2	28,4	28	28.8	28
Losses % P2O5				
Unattacked	1.2	1.5	0.9	0.9
Co-crystallized	1	1.26	0.8	1.2
Water soluble	0.6	0.7	0.6	0.7
Total yield on gypsum	97.2	96.5	97.1	97.2



PHOSPHORIC ACID UNIT BY DIPLO PROCESS

RIEME PLANT

FIGURE 17 - 20

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