R.P. DIPLO PROCESS

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1 - AIMS AND OBJECTIVES OF THE DIPLO PROCESS

The different phosphoric acid production processes actually and presently available all over the world have had to face, since they have appeared on the market, the continue demand of increasing capacities. These capacities have risen from less than 100 metric tons per day to more than one thousand metric tons per day now.

Generally this growth of the unit capacities has been easily obtained through progressive steps, by extrapolating the size of the equipments without any major problems, sometimes only by setting several units in parallel. (Morocco is building a 8 train plant for producing 4000 tpd P2O5).
But in the last past years, while the plant capacities were growing up, the energy saving necessity appeared and, in the same time, a general and unevitable decrease in the quality of the basic raw material could be noticed roughly in all the mine fields. When most of the wet phosphoric acid processes were operating rocks containing 32 % to 35 % P2O5 even though more, they have now to work with ores containing 30 % - 28 % P2O5 sometimes 26 % P2O5.

Everyone knows the influence of the different impurities that balance the P2O5 in the rocks. In major cases low grade rocks produce attack slurries of poor quality, much gypsum of bad filtrability and low P2O5 content of the product acid (26 to 28 %). How to raise that poor filtration keeping a product acid of 30 % P2O5 or more ?

Unground rocks, or slightly ground ones, require long residence time, are difficult to digest in a high grade acid and give important losses. How to reduce the losses, how to reduce investments and production costs, while producing the same 30 % P2O5 acid ?

To solve specific contingencies some tricky approches appeared such as hemihydrate or double crystallization from which Rhone Poulenc has choosen to stand aside until now. This RP position is to ensure that its plants will remain easy and reliable to run with the minimum costs.

Still developing its single tank process and its well-known UCEGO rotary table filter the RHONE POULENC group has been able, from its industrial experience and its continuing research, to develop a novel process meeting particularly the following ends :

- high P2O5 content of the product acid
- high filtering capacity
- high P2O5 yield
- ability to process low-grade rocks
- ability to use unground rock.

2 - REVIEW OF THE FUNDAMENTALS OF THE DIHYDRATE PROCESS

To describe the process, it is necessary to reconsider the laws ruling the attack of phosphates ; the analysis of these laws led to the choice of the single tank to carry out the reaction, and thus it is appropriate to recall the principles.

The main operating parameters in the sulphuric attack of phosphates are the P2O5 and H2SO4 concentrations, the solid material content and the temperature. These parameters are interdependent, and as soon as one or other of them is fixed, the operating range of the others is limited, and there is usually an optimum value. This means that stability of the run, with accurate control of the parameters, is of prime importance for a satisfactory attack of the phosphate.

2.1. Main operating parameters

* Slurry solids content

This parameter has less influence on the attack reaction, its main effect being on the stability. Too low a solid content reduces the reaction time pointlessly ; too high a solid content gives a slurry which cannot be pumped. A compromise value is used, which is slightly dependent on the temperature.

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* Temperature

The temperature affects the kinetics of the reaction ; a high temperature may be used to balance poor reactivity of certain phosphates. Nevertheless, other elements have to be considered, such as corrosion problems, scaling and the impurities content of the acid.

* H_2SO_4 concentration in the reaction medium

The best concentration values are a function of the reactivity of the phosphate rock. The specific area will give a first idea of that reactivity and, with the size distribution, will lead to determine the residence time.

A weak reactivity or a coarse size will be balanced by an increasing of the reaction volume. If not, the attack is unsteady, the H_2SO_4 consumption varies and reaches such a level that the attack is blocked (the well known phenomenon of the coating of the phosphate grains by the calcium sulphate due to the decreasing of the solubility of the sulphates).
Thus the sulphuric acid concentration will influence both the losses and the filtration rate.

The losses
- in unattacked form. An operating concentration too close to that which results in blocking the reaction leads to an increase in this form of P_2O_5 losses
- in co-crystallized form. Too weak a concentration favours the substitution of sulphate ions by phosphate ions in the gypsum crystal lattice. This becomes more marked when P_2O_5 concentration increases.

The filtration efficiency usually falls off if H_2SO_4 concentration is too weak.

It is also necessary to bear in mind that any sulphuric acid excess will appear in the product acid as a contaminant, increasing its bulk.

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* P2O5 concentration in the reaction medium

For all phosphates, the P2O5 concentration of the medium has a direct influence on the gypsum crystallization, the extent of which differs from one phosphate to another, depending on, among other things, the impurities loading in the acid. Generally, it can be said that the crystal quality, and hence the filtration efficiency, fall slowly as the P2O5 concentration is increased up to a certain point, beyond which the decline is drastic. The P2O5 concentration also influences the attack-speed ; thus, at a weak P2O5 concentration, the reaction time may be considerably reduced without prejudicial effect on the stability of the run.

Considering the effects of these different parameters on the attack result everyone knows that operating a phosphoric attack unit consists in adjusting an adequate compromise between the different values of the main operating parameters under control in the attack medium.
These are interdependent and as soon as the optimum set of parameters is obtained it is of prime importance to stabilize them under accurate control for a satisfactory attack of the rock. Rhone Poulenc has patented the principle of the single tank because it is obviously the best way to stabilize the attack conditions ; all the reacting volume is available to ensure this stability : the whole reaction medium circulates widely to smooth out any variation caused by the inlet of the raw material and the evolution of the products.

2.2. Main feature of the RP single tank process

Just a few words to make everyone well aware of the Rhone Poulenc dihydrate original process before entering ahead in the Rhone Poulenc Diplo system.

Single attack tank with single central agitation
with air cooling, improved by surface coolers
overflow to slurry pump transfering the slurry directly to the filter.

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Ucego filter rotating table filter, with no tilting pans that is quick drain, no dilution, little maintenance

Simplified filtrate circuits, simplified separators, no bottom tanks, short piping.

3 - RP DIPLO PROCESS

To simplify our account we will consider that the temperature and the solid content are fixed at any usual value in the dihydrate process (let say 78°C and 35 % solid) as their influence is less in their usual operating range than the one of the major operating parameters we previously pointed out : P2O5 content and H2SO4 excess of the product acid.

The table here summarizes the way these two parameters influence the losses and the filtration rate

results / actions	unattacked losses	cocrystallized losses	filtration rate
H2SO4 ↗	↗	↘	→
H2SO4 ↘	↗	↗	↘
P2O5 ↗	↗	↗	↘
P2O5 ↘	↘	↘	↗

These fundamental remarks led Rhone Poulenc teams to develop the "Diplo" process. This process is to be considered as an extension of the single tank Rhone Poulenc process. It is based on the principles of the single tank and retains all its advantages. The phosphate is attacked in several stages, usually two. This attack is carried out in tanks in series, each of them being considered as a single tank.

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Let us have a look at these diagrams that show the variation of the filtration rate of a slurry from different rocks and produced at different P205 contents of the product acid.

(appendix 4 and 5)

The two slides relate on rocks from the States. The first one was obtained from North Carolina rock 63 BPL and shows the important decrease in filtration rate when producing acid at 30 % P205 instead of 26 % ; roughly dividing by 2 the figure obtained at 26 %.

The second one shows variation of filtration rate versus P205 content of product acid for calcined IDAHO rock.

For sure this is not a discovery. But the Diplo process enable keeping a good filtration rate in a stronger acid. And here is the plus ! It is shown on the same diagram from 1 to 2 or A to B.

This sketch (appendix 6) shows the basic flow-sheet of a Diplo. It consists in producing the major part of the crystals from a low grade acid in the first reactor.The good quality slurry thus obtained overflows to the second reactor where the P205 content of the acid is raised, adding rock and sulphuric acid. The end slurry is then conveyed to the filter. Strong acid is partly sent to storage as the production, partly recycled to the second reactor to control the solid content of the reactor n° 2 ; the medium acid is recycled to the first tank, and conveys the process water, to control product acid grade, and the low grade acid, to control the solid content of the slurry.

Without presenting any boring calculation, it is to be clear to every one that the higher the amount of rock processed in the first tank at low P205 content the better the filtration rate on a one hand but at the same time the lower the amount of P205 available in the second tank to raise up the P205 content of the product acid on the other hand.

To illustrate that have a look at the following figures (theoretical ones) starting from the same P205 content of 27 % in the acid from the first tank the final one would be, along with the ratio of rock in each tank

rock ratio	60/40	75/25	90/10
% P205 increase	4.9	2.5	0.9

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Three other figures to show the influence of the solid content of the slurry in the first tank, again starting from 27 % and with 75/25 rock ratio

Solid content	30 %	35 %	40 %
% P2O5 increase	4.4	5	5.7

On the table showing the influence of P2O5 and H2SO4 content on the losses we have seen that when P2O5 is decreased and H2SO4 increased it is possible to improve the total attack recovery on unattacked and cocrystallized P2O5. The figures are not so spectacular as the ones of filtration rate, an example here from a pilot test :

single tank	29.15 % P2O5	97.5 % attack recovery
diplo system	29.95 % P2O5	97.9 % attack recovery

All this demonstrate the flexibility of the system. We have no time to go in all the routes possible with the Diplo ; I would just like to point out that using finally ground rock we don't fear increasing H2SO4 excess and blocking the attack and it is then possible to improve more the recovery by raising H2SO4 content in the first tank which is then reduced at normal level in the second one.

Before having a look to some industrial uses of the Diplo process we will try to summarize in a diagram the possibilities of the Diplo (appendix 9). The representative conditions prevaling in the Diplo process for each of these cases are shown on the table I andII.
Of course any combination can be envisaged to get at the same time an improvement of the P2O5 content of the product acid and of the recovery.

Table I

Conditions in high P2O5 recovery "Diplo" process

	Reactor 1	Reactor 2
Proportion of total feed %		
Phosphate rock	90	10
Sulphuric acid	100	
P2O5 content of acid, %	28	30
H2SO4 content of acid g/l	75	25
Particle size of phosphate, μ	400	600

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The advantage of this process is the increment in the yield, which can be some 1 % higher than that of a standard process giving 97 % attack yield. This process requires thorough grinding of the part of the phosphate supplied to the first tank.

Table II

Conditions in high concentration "Diplo" process

	Reactor 1	Reactor 2
Proportion of total feed, %		
Phosphate rock	70	30
Sulphuric acid	70	30
P2O5 content of acid, %	28	33
H2SO4 content of acid, g/l	25	25
Particle size of phosphate, μ	600	600

The advantage of this process is that it enables a filtering capacity to be attained which is usually more than twice that achieved with a standard process for the same concentrattion of product acid. It can be remarked that the slurry coming from the first tank, formed of crystals giving a very good filtration, introduces into the second tank such a quantity of crystals that the filtration quality is but very little modified there in spite of the difference in crystallization conditions. The yields is improved by the 1/2 point owing to the fact that 70 % of the crystallization is done in a diluted P2O5 medium.

4 - INDUSTRIAL EXPERIENCE

Two different units are presently operating using the RP Diplo process.

4.1. AZF Diplo plant

The oldest one has been commissionned in March 1974 in Grand Couronne, in France, for the APC Cy at that time. It is now operated by AZF, the fertilizer subsidiary of Charbonnages de France. Designed for 650 MTPD it has been producing 800 MPTD using 70 % BPL rock. The P2O5 content of the product acid has been up to 32 % while the recovery was over 97 %. In the recent past, producing 28.5 % P2O5 acid (they have an excess steam on the site) they achieveda recovery of 97.7 %.

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It is equiped with two tanks of 600 m3 each and a number 11 UCEGO filter of 153 m2 under vacuum, and has been basically designed as a Diplo process plant.

4.2. SICNG retrofitted plant

The second one, on the contrary, is the result of the retrofitting of two old single tank trains.
The first one was equiped with a 300 m3 tank, the second one with a 200 m3 tank and both operated a Prayon n° 18 B filter. They were producing together someting like 250 to 300 MTPD P205. Due to the poor conditions of the PRAYON filters and the consequent bad results, it has been decided to install a new UCEGO n° 7 filter just taking place of one of the Prayon and at the same time to boost the output by using the two existing tanks in a Diplo train, the 300 m3 tank as first tank, the 200 m3 as the second tank and an unique filter, the UCEGO one of 63 m2 under vacuum. The output using unground Taïba rock was 360 MTPD with a 97 % recovery.
Recent figures while using 400 microns (35 mesh Tyler) prescreening of the rock and reincorporating the ground oversize show a recovery around 97.3 % under normal operation. (I want to say"not under a typical controled guarantee test period").

4.3. Economics

What about economics ?
As a preamble I would like to emphasize the fact that any comparison between Single tank system and Diplo one is dependent on the fundamental objective choosen. For an importing country, with no rock, savings on recovery is of prime interest ; for somebody else energy savings would be the main objective. And from that objective the design and the economic balance will be different by the fact.
The following figures relate to a preliminary study we made with a French engineering company, Krebs Cy, which has been working many years with the RP process. They apply to a 900 tpd unit for an importing country and processing Florida and Morocco rocks.

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On the investment cost and on french basis evaluation, here are the relative figures :

900 MTPD single train	Florida	Morocco
single tank	100	86.3
Diplo	101.3	88.5

On the major utility consumption the figures are as follow for 900 MTPD.

	Florida		Morroco	
	S.T.	Diplo	S.T.	Diplo
Power kWh/t P2O5	149.5	151.6	103.2	102.6
Steam (LP) t/t P2O5	2.13	1.6	1.94	1.6

Neglecting the power the main saving is on the steam, between 100 000 and 150 000 Mtpa. In term of cost it depends on whether the steam is used for power generation or not.

For both rocks the expected gain on the overall recovery of the attack and evaporation was 0.5 %.

This rock saving represents some 1500 Mtpa P2O5. This is a rather small amount for a Floridan fertilizer Company having its own mine, but evaluated by an importing country Company it may me appreciated.

Considering the price of such a plant and the prices of raw material and steam the pay back time is a bite more than a year on the raw material and only 6 weeks to 2 months on raw material and steam savings.

5 - CONCLUSION

For a very small investment extra cost choosing the Rhone Poulenc Diplo system, one can have in hands the most flexible plant, either retrofitted or newly built, operating along reliable process and technology, proven all over the world for many years with all the rocks.

" D I P L O "

A I M S   A N D   O B J E C T I V E S

- High P2O5 content of product acid

- High filtering capacity

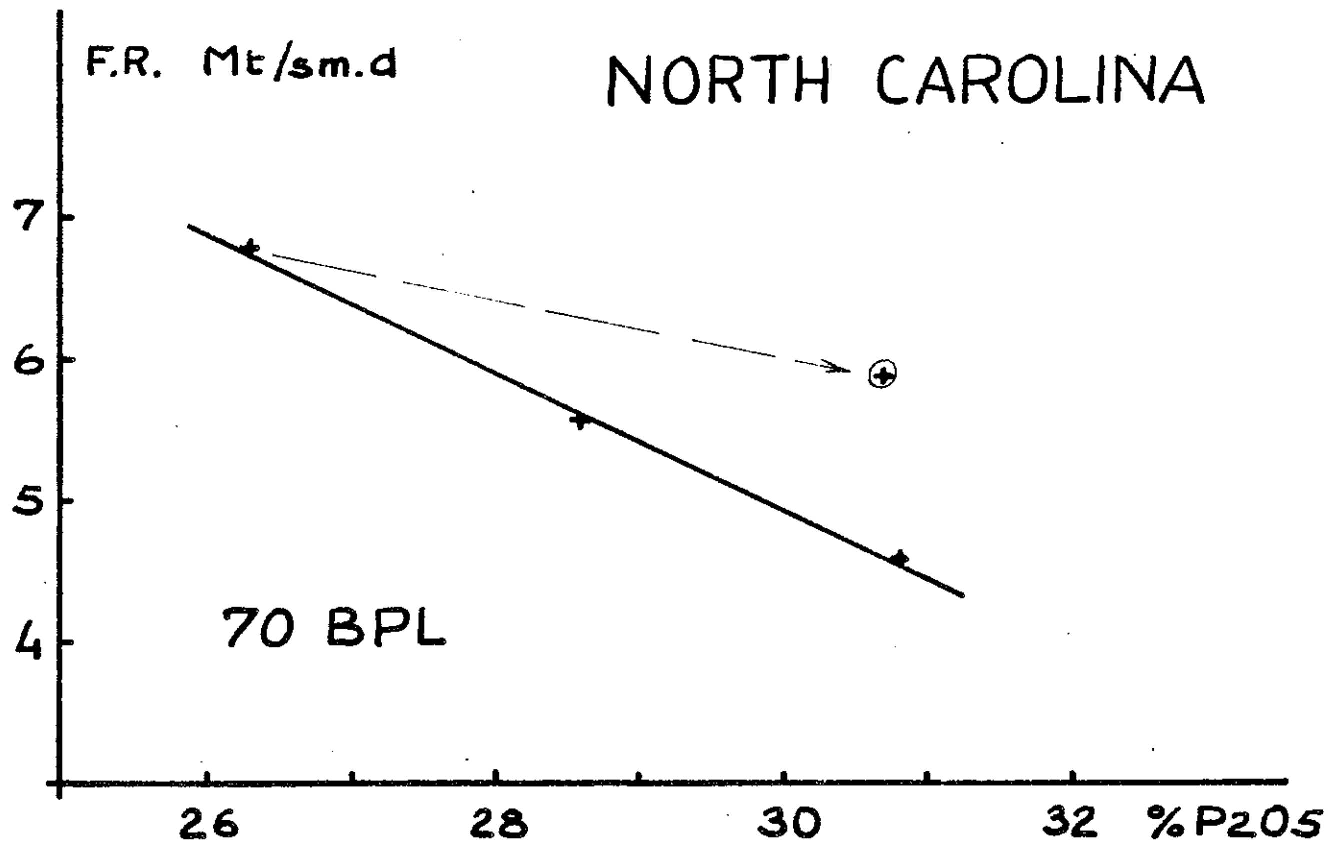
- High P2O5 yield

- Ability to process low-grade rocks

- Ability to use unground rock

A T T A C K   P A R A M E T E R S

- Temperature of the slurry
- Solid content of the slurry
- H2SO4 content of the liquid phase
- P2O5 content of the liquid phase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NORTH CAROLINA
7
6
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70 BPL
26
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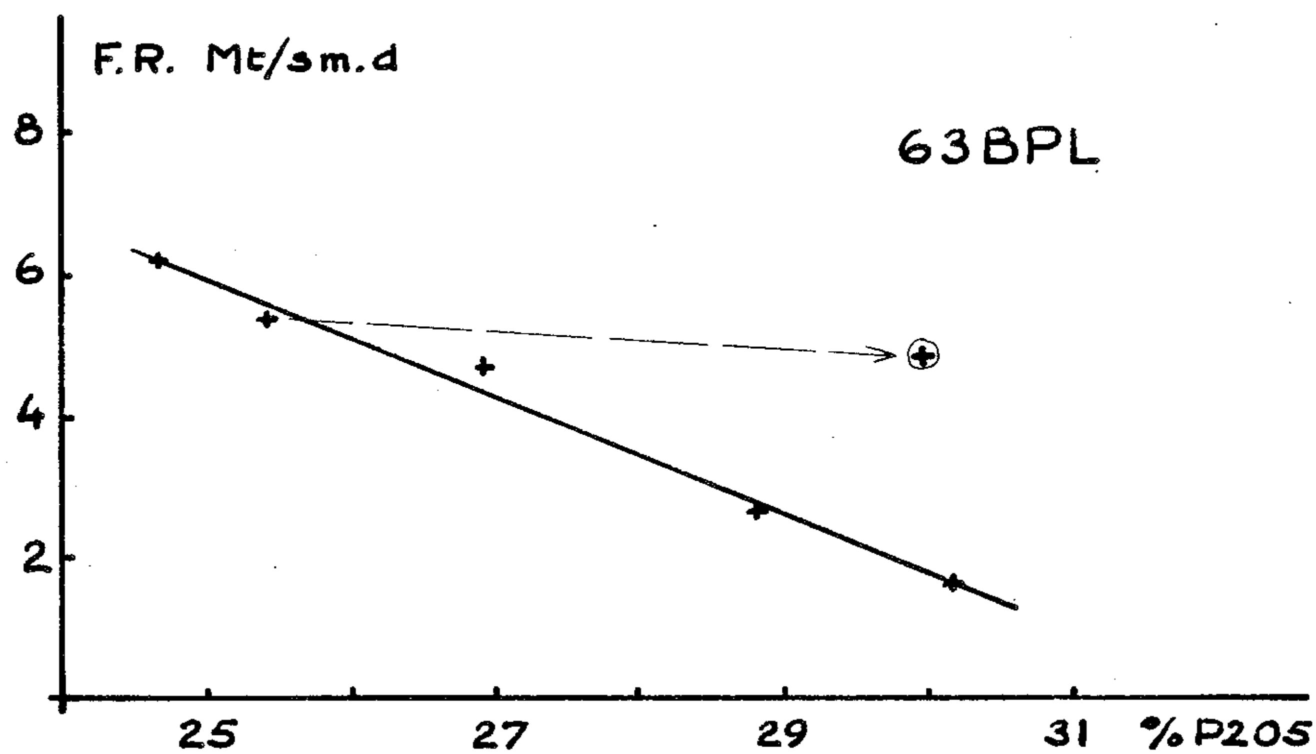
%P2O5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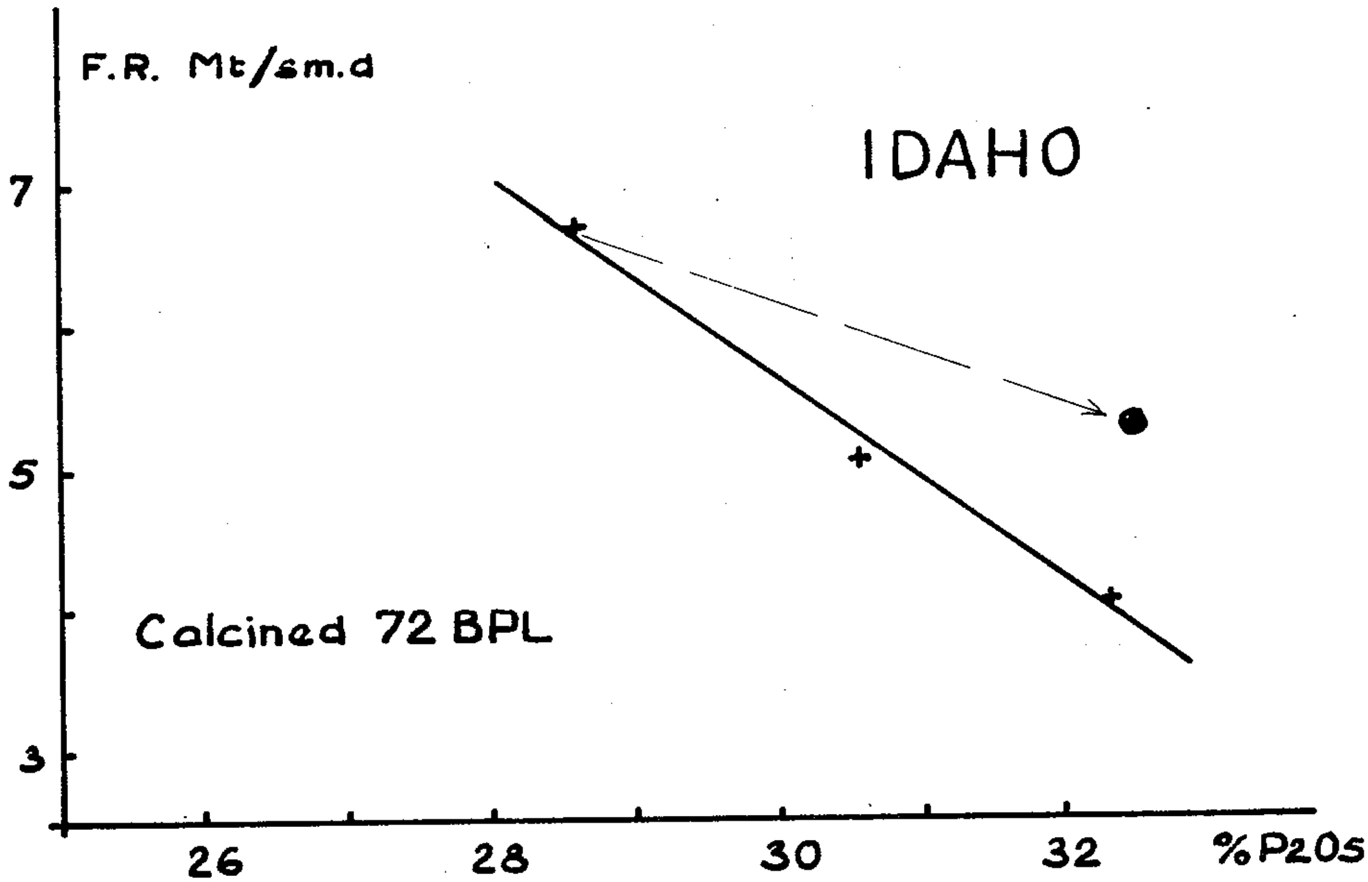
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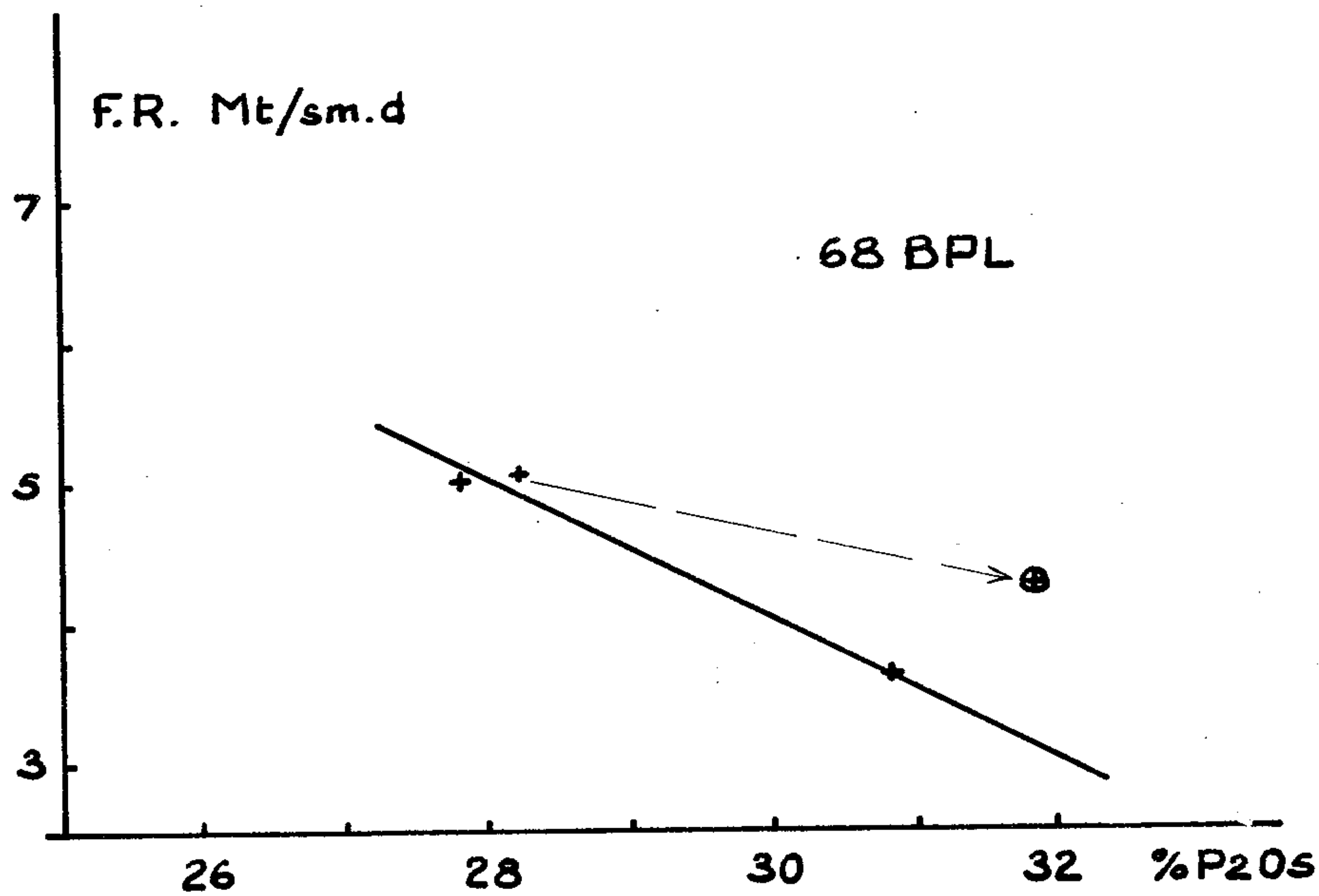
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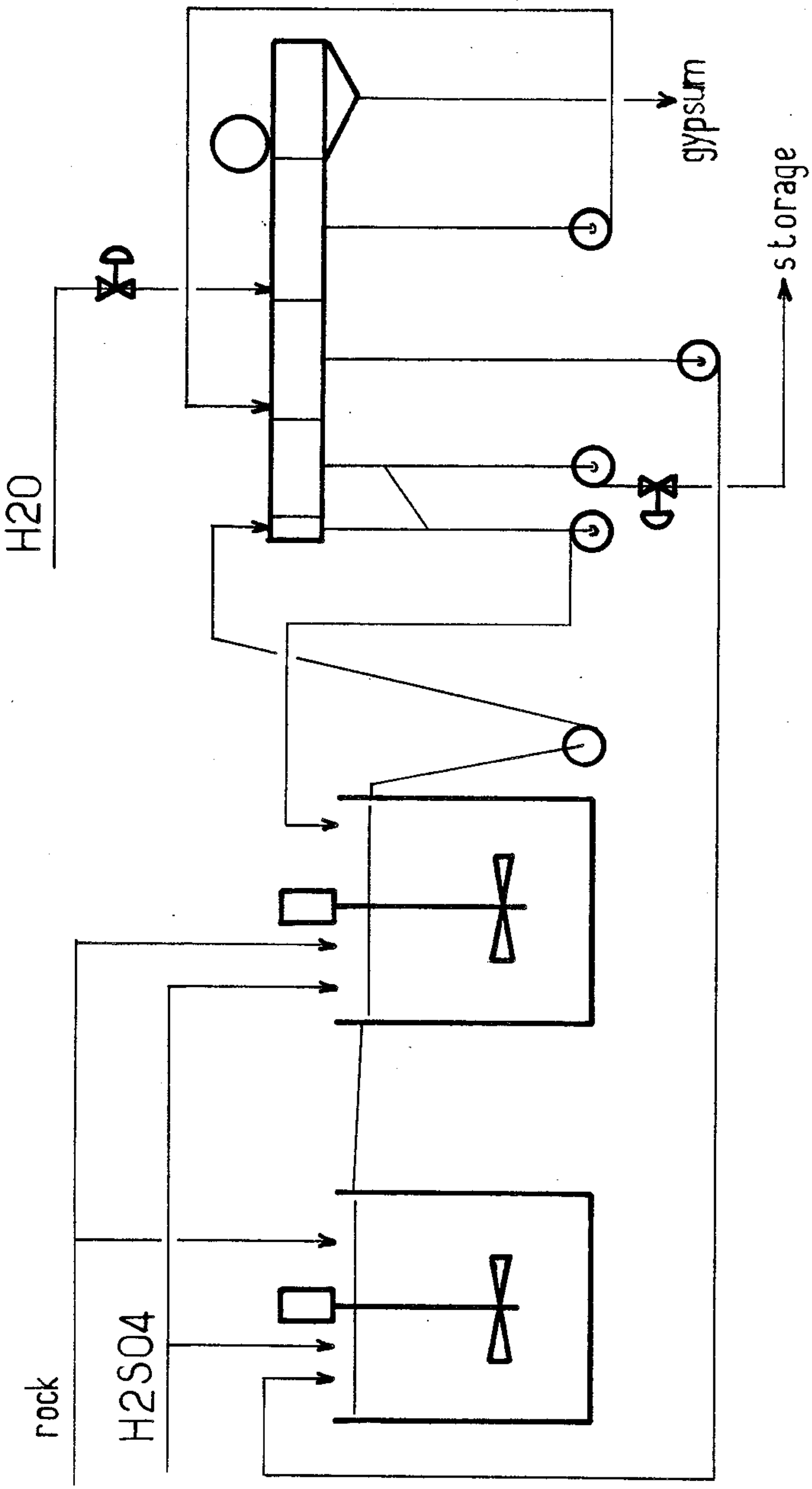
gypsum
storage
H2O
rock
H2SO4

rock ration 1/2	60/40	75/25	90/10
P205 increase (% point)	4.9	2.5	0.9

Solid content first tank %	30	35	40
P205 increase	4.4	5	5.7

Diplo
slide 8

	P2O5 content product acid %	Attack recovery %
Single tank system	29.15	97.5
Diplo system	29.95	97.9

High P205

Standard		DIPLO
↘	Recovery	→
↘	Filterability (output)	→

High recovery

Standard		DIPLO
↘	P205 content	→
↘	Filterability (output)	→