

PRAYON PROCESSES FOR PHOSPHORIC ACID PRODUCTION

Prayon
Technologies

Our ideas make profitable plants



www.prayon.com

TABLE OF CONTENTS

PRAYON TECHNOLOGIES: THE REFERENCE IN THE PHOSPHORIC ACID WORLD	05
THE CHARACTERISTICS OF PRAYON TECHNOLOGIES	06
A process for each situation	06
Production-oriented	06
Flexibility	06
Efficiency	06
World wide references	06
CALCIUM SULPHATE CRYSTALLISATION PHASES	07
PRAYON TECHNOLOGIES PROCESSES	08
First range: process with the first reaction as “dihydrate”	08
Second range: process with the first reaction as “hemihydrate”	08
FEATURES OF PRAYON TECHNOLOGIES DESIGN	10
Reactor design	10
Sulphate gradient of the slurry in the attack tank	10
Low Level Flash Cooler (LLFC)	11
Agitators	12
Filters	13
PRAYON TECHNOLOGIES PROCESSES WITH INITIAL DIHYDRATE REACTION	14
The Mark 4 Dihydrate Prayon Process (DPP)	14
The Central Prayon Process	15
The two-crystal process (DA-HF)	16
Very adapted to DH revamping	17
PRAYON TECHNOLOGIES PROCESSES WITH INITIAL HEMIHYDRATE REACTION	18
Three-crystal process or PH3 (Prayon Hemihydrate 3-crystal)	19
Two-crystal process or PH2 (Prayon Hemihydrate 2-crystal)	20
One-crystal process or PH1 (Prayon Hemihydrate 1-crystal)	21
PRAYON RELATED TECHNOLOGIES	22

PRAYON TECHNOLOGIES

THE REFERENCE IN THE PHOSPHORIC ACID WORLD

For over 60 years, PRAYON TECHNOLOGIES s.a. has been a leader in the licensing of phosphoric acid processes.

- + Plants using the Prayon technology produce the majority of the world tonnage of phosphoric acid.
- + Prayon technology and equipment have been used in over 145 plants located in over 30 countries.
- + Dozens of different phosphate rocks have been used in plants from 25 to 2000 mtpd P₂O₅.

This worldwide success in licensing is not accidental. Rather, it is based on experience gained in the area of production. Behind PRAYON TECHNOLOGIES s.a. is its parent company Prayon s.a., a production company founded in the 19th century, which has been manufacturing phosphoric acid and phosphates for more than sixty years.

The Prayon Group has 4 production sites, a total of about 1400 employees, and an annual turnover of about 700 million EUR.

PRAYON TECHNOLOGIES mission is to licence the processes developed in-house, **“by a producer for producers”**.



● Worldwide presence of Phosphoric Acid Technology

THE CHARACTERISTICS OF PRAYON TECHNOLOGIES

A PROCESS FOR EACH SITUATION

PRAYON TECHNOLOGIES offers 6 different processes, each one with its own characteristics. This range ensures that we can provide you with the process which best meets your requirements.

PRODUCTION-ORIENTED

PRAYON TECHNOLOGIES is a subsidiary of a manufacturing company. Prior to being made available on the market, all technologies and equipment are tested and proven at our production facilities.

FLEXIBILITY

Plants designed by PRAYON TECHNOLOGIES achieve excellent results. They operate successfully with a large number of phosphate rocks of various origins and qualities, including the lowest grades. Also, if required, the plant can be optimised using phosphate blends.

EFFICIENCY

PRAYON TECHNOLOGIES processes enable plants to achieve higher efficiency than their competitors, due to the unique design of the multi-compartmented reactor. This design allows the raw materials to be introduced at the most effective point in the reactor, yielding optimal results.

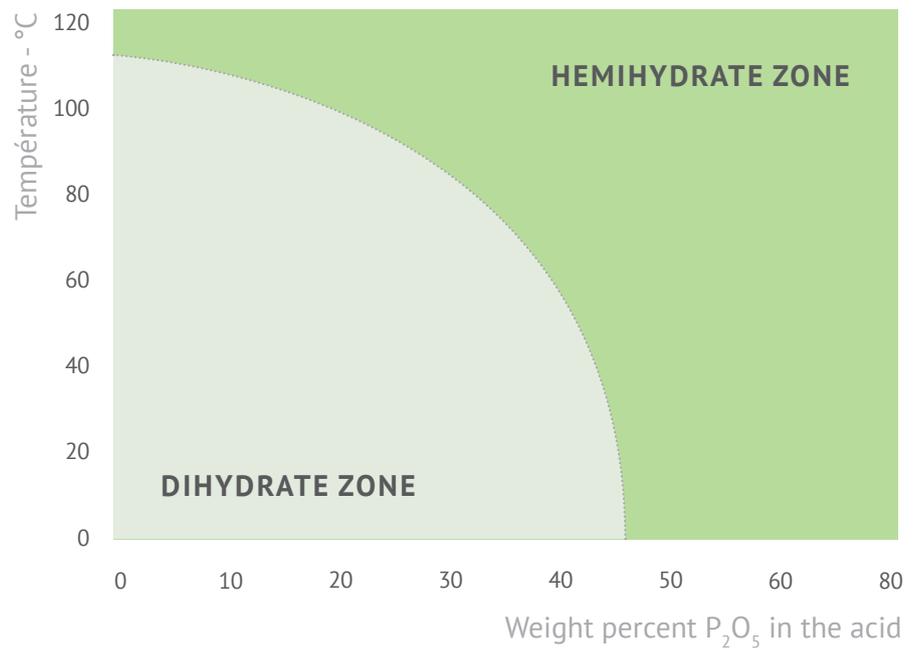
WORLD WIDE REFERENCES

These various features have enabled us to sell a total of over 130 units, including more than 50 repeat orders. The latest large scale projects in the world are based on most advanced Prayon technologies.



CALCIUM SULPHATE CRYSTALLISATION PHASES

The main reaction of phosphate rock with sulphuric acid produces phosphoric acid and calcium sulphate. Depending upon the physical and chemical conditions of the reaction, the calcium sulphate may take the form of dihydrate, α -hemihydrate or anhydrite.



PRAYON TECHNOLOGIES PROCESSES

Prayon Technologies processes can be divided into two groups :

FIRST RANGE

Processes with the first reaction as “dihydrate”

+ With one crystal: “Dihydrate” Prayon Process or DPP (Mark 4)
DPP **DIHY** > Dihydrate

+ With two crystals: “Dihydrate then Hemihydrate” Central-Prayon Process or CPP
CCP **DIHY** > **HEMI** > Hemihydrate

+ With two crystals and only one filtration: “Dihydrate - hemihydrate filtration” or DA-HF.
DA-HF > **DIHY** **HEMI** > Hemihydrate

For the past 30 years, Prayon’s licensing activities have been mainly based on the DPP - Mark 4 dihydrate process for phosphoric acid production. Its ability to efficiently convert various types of phosphates, its flexibility, its ease of operation and its low maintenance cost make it the leading process on the market.

As calcium sulphate is sold at the Prayon production site at Engis (Belgium), the purity and quality of the gypsum must be

very high. To fulfil these requirements, the process used at our unit is the two-stage dihydrate hemihydrate CPP or CENTRAL-Prayon Process.

This high-efficiency process (approx. 98.5% cake efficiency) can produce a relatively strong acid (+/- 35% P₂O₅).

The DA-HF is the newcomer, it ensures a high efficiency with an investment cost close to a Dihydrate Process.

SECOND RANGE

Processes with the first reaction as “hemihydrate”

+ With one crystal: “Hemihydrate” Prayon Process or PH1
PH1 **HEMI** > Hemihydrate

+ With two crystals: “Hemihydrate” then “Dihydrate” Prayon Process or PH2
PH2 **HEMI** > **DIHY** > Dihydrate

+ With three crystals: “Hemihydrate” then “Dihydrate” then “Hemihydrate” Prayon Process or PH3
PH3 **HEMI** > **DIHY** > **HEMI** > Hemihydrate



In the late 1970s, the increase of oil prices put pressure on Prayon to develop higher strength processes, and two alternatives were considered. First, the development of a process with hemihydrate as the first stage, to produce 43-46% P₂O₅ acid, or changing the operating conditions of the existing Central-Prayon plant to achieve a product acid strength higher than the 34-36% obtained at that time. This solution was intended to produce merchant grade gypsum with similar qualities to that obtained previously.

A single-stage HH process could not achieve the gypsum quality required by the downstream plaster producer, nor a high enough efficiency to produce phosphoric acid economically at the inland European site.

Although a two-stage hemihydrate-dihydrate process would have been more efficient, the drying stage would have been costly, compared to the self-drying characteristics of hemihydrate which cause the free water to be absorbed during hydration.

A novel process was then developed, a Hemi-Di-Hemi process with two recrystallisation stages and two filtration stages. This process was named the ‘Prayon Hemihydrate 3-crystal process’ or PH3, and can produce a 46% P₂O₅ acid with over 98.5% process efficiency and high quality calcium sulphate.

Under less stringent conditions, where gypsum quality is not so critical, the final stage of the PH3 process can be deleted, leading to a hemihydrate-dihydrate process. This type of process was developed for licensing purposes and is known as the “Prayon Hemihydrate 2-crystal process” or PH2. This process can yield a 43-46% P₂O₅ acid and has a process efficiency of over 98.5%.

In cases where lower efficiencies are acceptable, the removal of the dihydrate stage leads to a single-stage hemihydrate process known as PH1. This can yield acid 39-45% P₂O₅, with a process efficiency of up to 95%. If lower strengths are acceptable, efficiency can be increased. Alternatively, higher strengths can be achieved at the expense of efficiency.

COMPARISON OF PRAYON PROCESSES (TYPICAL VALUES)

Characteristics of the process	Mark 4	CPP	DA-HF	PH3	PH2	PH1
Solids product type	Dihydrate	Hemihydrate	Hemihydrate	Hemihydrate	Dihydrate	Hemihydrate
Product acid: % P ₂ O ₅	28.5	34 to 36	32 to 36	43 to 46	43 to 46	39 to 45
Product acid: % SO ₃	1.5	0.6 to 1.2	2 to 3%	0.6 to 1.2	0.6 to 1.2	0.6 to 1.2
Efficiency %	95 to 96	> 98.5	97 to 98	> 98.5	> 98.5	92 to 95
Analysis of the calcium sulphate						
(On dry basis 50°C) Free H₂O %	18 to 20	14 to 20	14 to 20	14 to 20	16 to 20	14 to 20
(On dry basis 250°C)						
Crystal H ₂ O %	20.5	6.2 to 6.5	6.2 to 6.5	5.4 to 5.8	18 to 19	6.5
Total P ₂ O ₅ %	0.8 to 1	0.25 to 0.35	0.35 to 0.65	0.15 to 0.25	0.25 to 0.35	1.2 to 1.8
W.S. P ₂ O ₅ %	0.2 to 0.3	0.1 to 0.15	0.1 to 0.2	0.05 to 0.1	0.05 to 0.1	0.2 to 0.3
UNR. P ₂ O ₅ %	0.05 to 0.1	0.05 to 0.1	0.05 to 0.1	0.05 to 0.1	0.05 to 0.1	0.05 to 0.1
Cocryst P ₂ O ₅ %	0.5 to 0.6	0.1 to 0.2	0.1 to 0.2	0.05 to 0.1	0.15 to 0.25	0.8 to 1.4
CaO %	39.8	39.7	39.7	40.6	39.8	39
SO ₃ %	56.9	57	57	58	57.4	54.9
F%	0.5 to 0.8	0.4 to 0.6	0.4 to 0.6	0.1 to 0.2	0.5 to 0.7	1 to 1.2
Na ₂ O%	0.4 to 0.8	0.3 to 0.6	0.3 to 0.6	0.1 to 0.2	0.3 to 0.6	1 to 1.2

FEATURES OF PRAYON TECHNOLOGIES DESIGN

In order to improve the overall performance of phosphoric acid plants, PRAYON TECHNOLOGIES continually updates the design of the equipment used in the process to improve recovery, energy efficiency and the operability of the plant.

REACTOR DESIGN

The PRAYON TECHNOLOGIES reactor design is unique. It is proven to be highly reliable. Its multi-compartments design allows flexibility and easy control of the sulphate in the attack section, which reduces P_2O_5 losses in the calcium sulphate and increases the profitability of the unit.

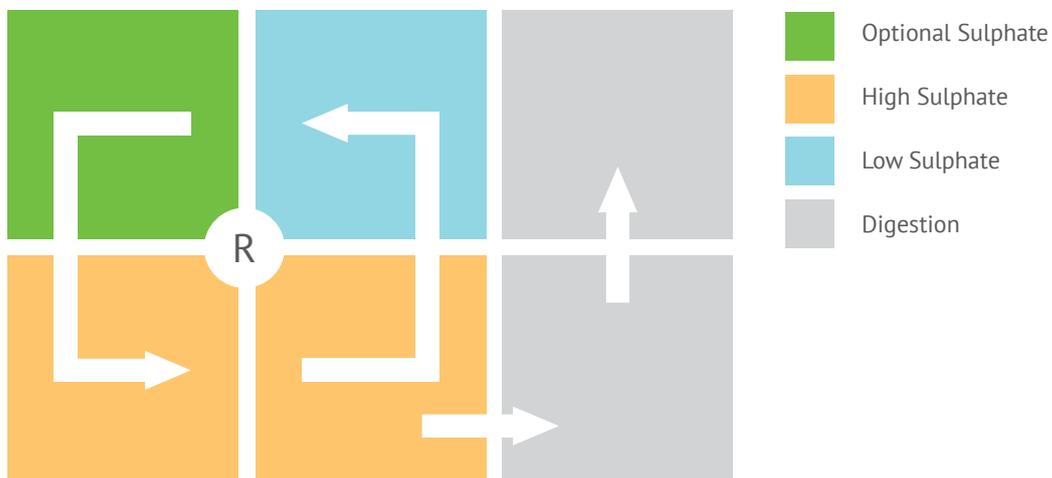
SULPHATE GRADIENT OF THE SLURRY IN THE ATTACK TANK

Two types of insoluble losses are produced during the production of phosphoric acid. These are the cocrystallised and the unreacted losses. The level of

each loss in the gypsum is a function of several parameters including the sulphate concentration in the reactor. When the sulphate concentration of the reaction slurry is high, cocrystallised losses are low. When the concentration is low, unreacted losses are low. In the reaction tank, rock is added in the first compartment. As sulphuric acid is not added to this compartment, the sulphate concentration is low. This results in the dissolution of the rock in a media where unreacted losses are low. In the compartments 2 and 3, sulphate concentration is gradually increased to reduce the cocrystallised losses. The design of the reaction tank thus minimises the insoluble losses. The level of sulphate gradient from one zone

to the other can be adjusted depending upon the process parameters and the origin of the phosphate rock.

After leaving the attack section, the slurry flows into the digestion section, where it will desaturate before being fed to the filter. Consequently, the gypsum crystals will be large and the slurry will be desaturated. This feature significantly reduces filter scaling, which enables the plant to be run for longer periods between washes. The increase in stability improves the overall recovery of the unit and the onstream time and thus increases the return on investment.



LOW LEVEL FLASH COOLER (LLFC)

The reaction of phosphate with sulphuric acid and the dilution of sulphuric acid are exothermic. To avoid boiling inside the reactor and to obtain the desired calcium sulphate crystals (gypsum or hemihydrate), the reaction slurry must be cooled. From the beginning, flash cooling has been a part of the Prayon process. This has proved to be more accurately controllable than air cooling, especially when the cooling rate must exceed nominal capacity.

The principle of operation is the following: the LLFC is a vacuum chamber into which the hot slurry is pumped. The water in the slurry begins to boil, causing water to evaporate from the slurry and thus cooling the slurry. In order to reduce scaling, the temperature difference between the inlet and the outlet of the LLFC is low (about 2°C or 4°F). This means that for efficient cooling the flow through the LLFC must be very large. This is ensured by a high flow rate axial flow pump with a low head and a low power consumption.



REACTOR AND LOW LEVEL FLASH COOLER

FEATURES OF PRAYON TECHNOLOGIES DESIGN

AGITATORS

Agitation is a key factor in chemical processes as it improves the mass transfer of the reagent and crystallisation conditions in the reaction slurry.

During the reaction period of phosphoric acid production, agitation is used for the following purposes:

- + To keep the solids suspended.
- + To renew the liquid layer (reagent) on the phosphate grains.
- + To break the foam on the surface of the reactor.

To be economical this process needs to be performed with as low a power consumption as possible. PRAYON TECHNOLOGIES has developed a special type of agitator to fulfil these requirements.

The bottom blade is a helicoidal shape to ensure a high pumping rate. It keeps solids suspended and the compartment clean. The middle blade is a pitched blade with a pumping effect. It also generates shear, which improves the mass transfer and the incorporation of the reagents. The top blade is a vertical turbine blade with an antifoaming effect (achieved by splashing liquid on the reactor surface) and helps incorporate reactants fed to the surface of the reactor.

In the digestion section, strong agitation is no longer necessary. Only helicoidal blades with low specific power consumption are used.

For a few years now, PRAYON TECHNOLOGIES has been using a Computerized Fluid Dynamics software in order to further improve the design of its agitators.



PRAYON REACTION TANK AGITATOR

FILTERS

The Prayon tilting pan filter is the best known filter in the phosphoric acid industry. Its washing efficiency is the highest of all the filters available on the market. Recent developments in filter technology, such as the “fast-drain” cell, the central valve, inverting track design, etc., have improved its operability, reduced maintenance cost and increased the filtering surface to the total surface ratio.



PRAYON TILTING PAN FILTER

PRAYON TECHNOLOGIES PROCESSES WITH INITIAL DIHYDRATE REACTION

THE MARK 4 DIHYDRATE PRAYON PROCESS (DPP)

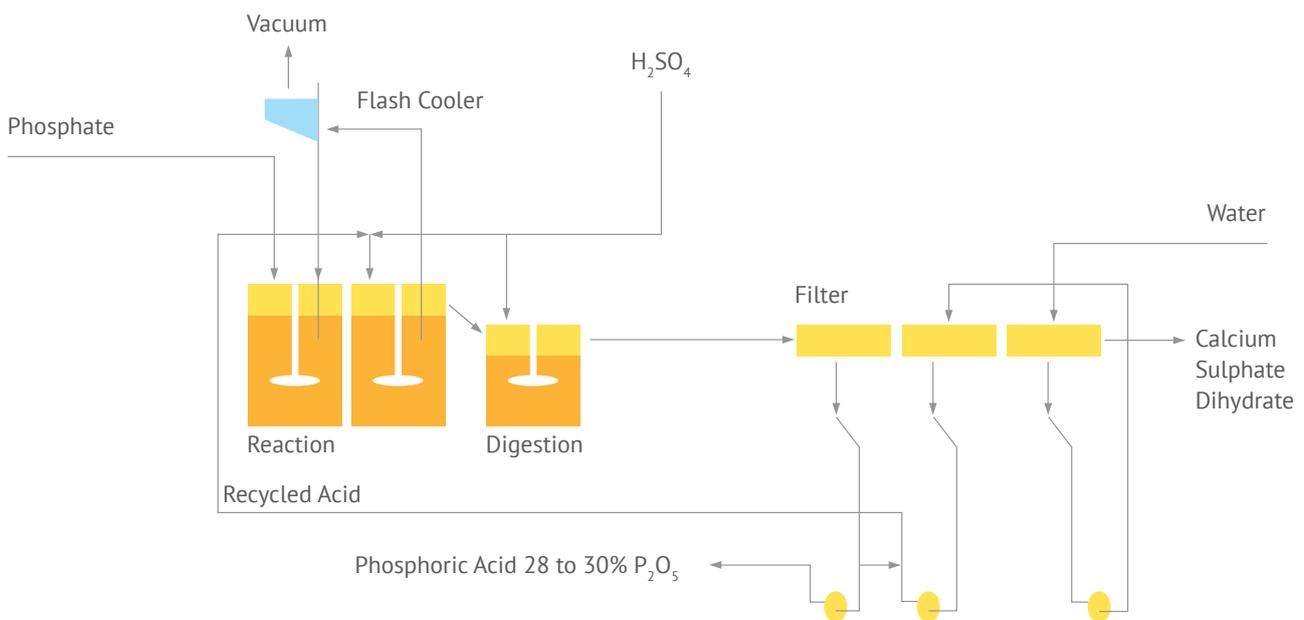
This process has undergone major innovation every ten years or so, up to the achievement of the highly efficient Mark 4 version, which is a favourite with producers due to its reliability, simplicity of operation and the use of tried-and-tested equipment.

THE MAIN CHARACTERISTICS OF THE PROCESS ARE

- + low investment and running costs
- + the ability to process all types of phosphates (sedimentary and igneous)
- + accepts phosphate slurry feeding (wet grinding)
- + water balance is easy to control (recycling of pond water, reduction and/or elimination of liquid effluent)
- + dihydrate route
- + good P_2O_5 recovery

RECOMMENDED FOR LOCATIONS

- + with low to medium cost rock
- + with low-cost energy (steam)
- + with gypsum disposal possibility



DIHYDRATE

THE CENTRAL-PRAYON PROCESS

The Central-Prayon Process was developed to produce a calcium sulphate (phosphogypsum) which could replace the natural gypsum in different applications.

This process is a dihydrate-hemihydrate process. During the first stage, slurry containing dihydrate crystals is produced. From that flow, the quantity corresponding to the product acid is sent to storage, the remaining quantity being sent with the solids to the conversion tank. In this reactor, sulphuric acid and steam are added to transform the

dihydrate solids into hemihydrate liberating most of insoluble losses. The slurry produced is then filtered and the cake washed. All filtrates from the second filter are recycled to the reaction tank, while solids can be neutralised and used as a raw material for gypsum products.

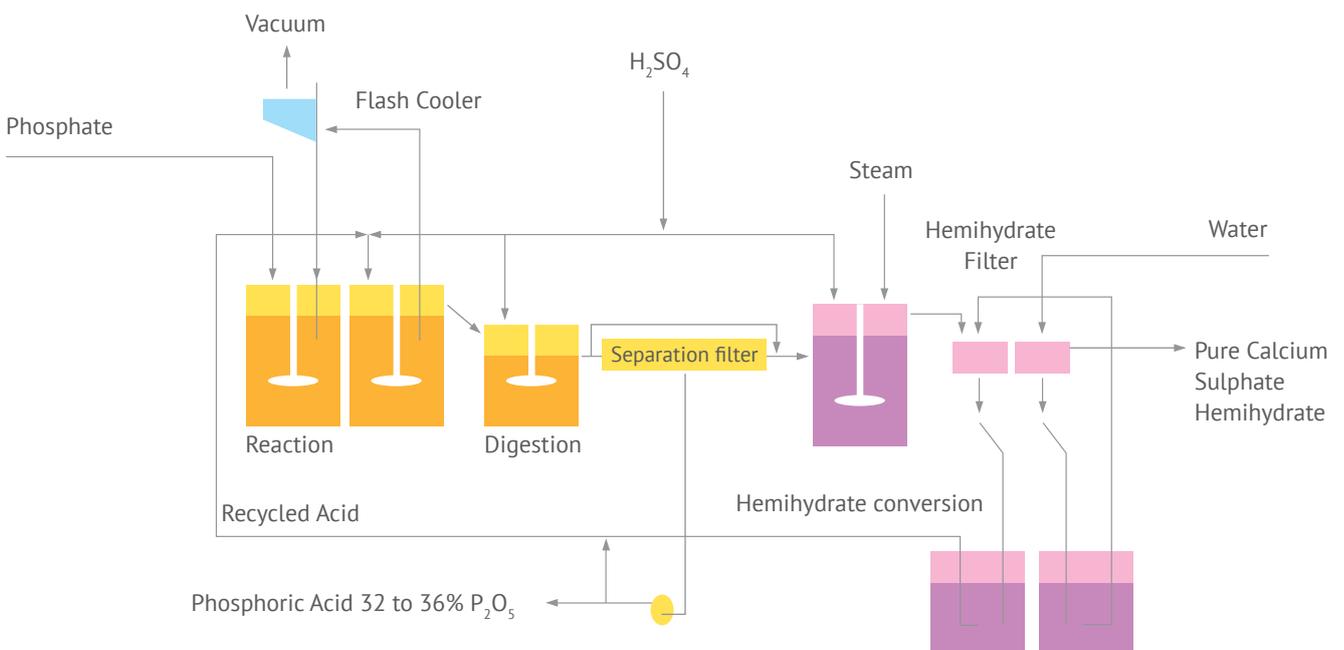
THE MAIN CHARACTERISTICS OF THIS PROCESS ARE

- + it produces a higher acid strength than DPP with much higher P₂O₅ recovery
- + it can process both types of phosphates: sedimentary and igneous

- + it produces CaSO₄.1/2H₂O which is self-drying due to its chemical properties and is purer than dihydrate, and can therefore be used directly as a merchant grade raw material (phosphate selection may be important)

RECOMMENDED FOR LOCATIONS

- + with medium - high-cost rock
- + with high-cost energy
- + with disposal limitation and/or with a potential market for this purer gypsum



DIHYDRATE

HEMIHYDRATE

TWO-CRYSTAL PROCESS OR DA-HF (DI ATTACK AND HEMI FILTRATION)

The Prayon DA-HF process® for producing phosphoric acid by sulphuric acid attack of natural phosphate rocks is a modern process leading to high P₂O₅ yield and giving, as a by-product, hemihydrate calcium sulphate. Dihydrate calcium sulphate is produced in the attack section where the phosphate is attacked by sulphuric acid. Then, the gypsum slurry recrystallizes into hemihydrate calcium sulphate in the conversion section before being filtered to produce the phosphoric acid.

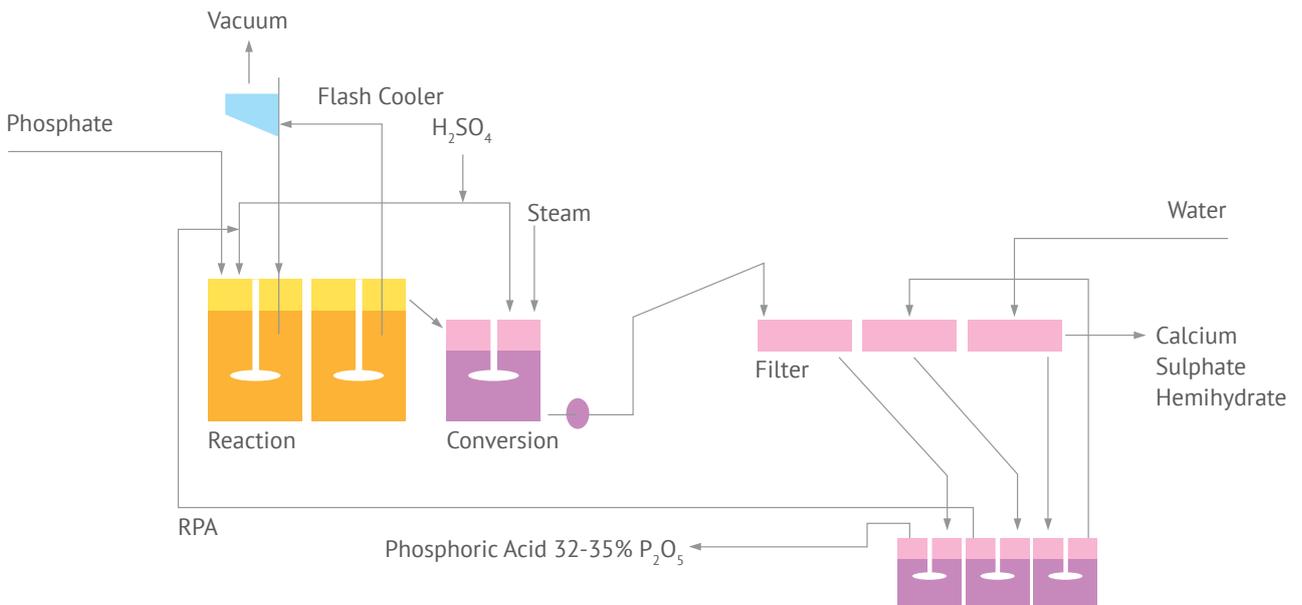
This process has been developed to produce phosphoric acid with a high P₂O₅ content (about 32 -35%) while only one filtration step is required.

THE MAIN CHARACTERISTICS OF THE PROCESS ARE

- + high strength phosacid
- + high P₂O₅ recovery (97.5-98%)
- + reduced CAPEX for high efficiency process
- + self-drying gypsum

RECOMMENDED FOR LOCATIONS

- + to adapt current Dihydrate process plant and improve profitability
- + with medium high-cost rock
- + with potential market for gypsum



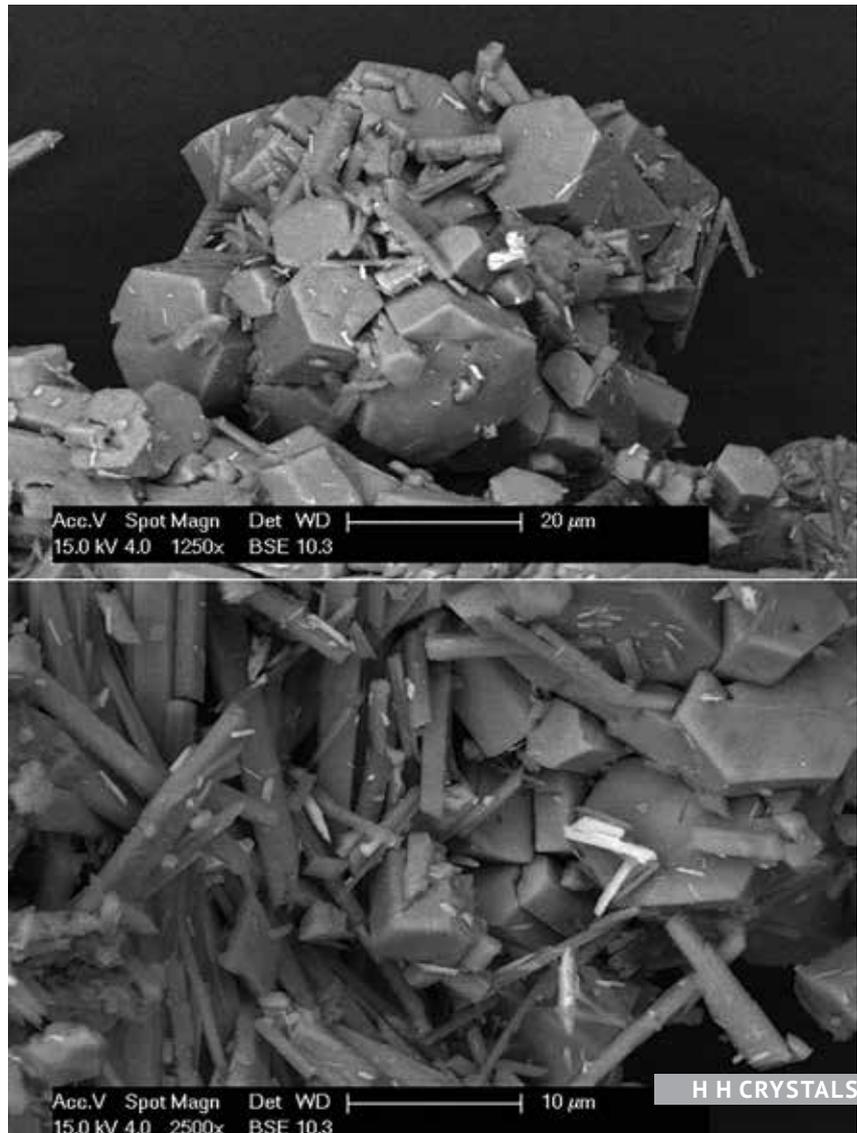
DIHYDRATE

HEMIHYDRATE

VERY ADAPTED TO DH REVAMPING

In case of Dihydrate plant revamping, this process is well adapted since:

- + The acid being more concentrated, concentration section does not need to be revamped;
- + Reactor volume can be kept as it is;
- + Conversion tank volume is small and can be installed near-by the existing equipment.



PRAYON TECHNOLOGIES PROCESSES WITH INITIAL HEMIHYDRATE REACTION

As energy costs weigh increasingly heavily, it may be worth producing a more highly concentrated acid directly from the filter, provided this is permitted by the water balance.

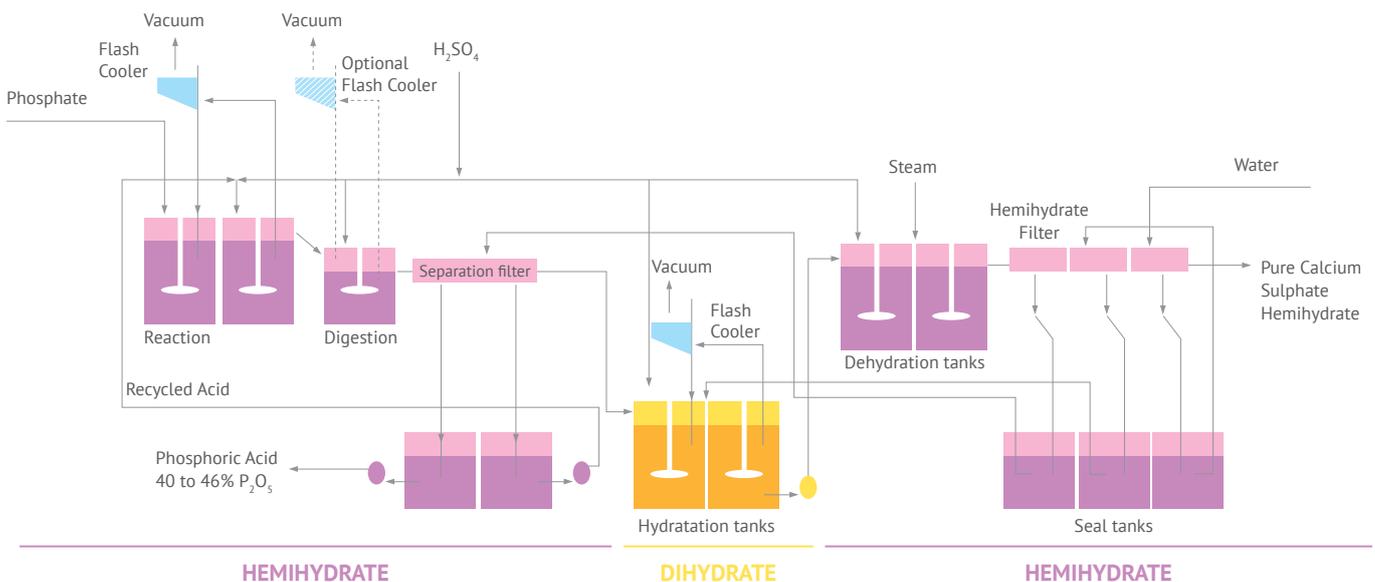
To fulfil this requirement, as well as that of producing a self-drying hemihydrate, Prayon has developed the PH3 process. This is a three-crystal process that yields a high P_2O_5 acid and a phosphogypsum that can be used as a base for construction materials. Once this process had been developed, we felt it could be simplified by deleting stages to fit to certain client requirements. This led to the development of two further hemihydrate processes.

To achieve a successful engineering package for high-strength processes, Prayon was able to rely on both:

hardware: many years of experience in the operation and engineering of equipment (reaction tank, agitators, cooling equipment, filters...)

software: our expertise with multicrystal process operation, our in-depth knowledge of phosphate behaviour and the ability to design successful industrial units based on pilot-plant data.

THREE-CRYSTAL PROCESS OR PH3 [PRAYON HEMIHYDRATE 3-CRYSTAL]



This process is divided into three stages:

Stage 1

α-hemihydrate attack-filtration:

The phosphate rock is digested in conditions which ensure the production of 43-46% P₂O₅ acid with low SO₃ (± 1%). The control of the operating conditions allows the production of hemihydrate which will filter rapidly and lend itself to full rehydration during the second stage.

Stage 2

Conversion of α-hemihydrate to dihydrate:

By changing the operating conditions (temperature, % P₂O₅, % SO₃), α-hemihydrate is converted into dihydrate in order to achieve a first purification, especially of unreacted and cocrystallised P₂O₅.

Stage 3

Conversion of dihydrate to α-hemihydrate and final filtration:

Operating conditions are modified to transform the dihydrate into α-hemihydrate. The slurry produced is then filtered. This step is similar to the second part of the Central-Prayon Process and aims at producing a high purity calcium sulphate which is separated by filtration and washed with water. If requested, the hemihydrate can be processed further (neutralisation, rehydration to produce a dry solid) to produce a substitute for natural gypsum.

THE MAIN CHARACTERISTICS OF THE PROCESS ARE

- + high P₂O₅ recovery (> 98.5%)
- + high-strength phosacid
- + self-drying gypsum

The last two points reduce energy consumption.

RECOMMENDED FOR LOCATIONS

- + with medium - high-cost rock
- + with high-cost energy
- + without easy gypsum disposal

PRAYON TECHNOLOGIES PROCESS WITH INITIAL HEMIHYDRATE REACTION

TWO-CRYSTAL PROCESS OR PH2 [PRAYON HEMIHYDRATE 2-CRYSTAL]

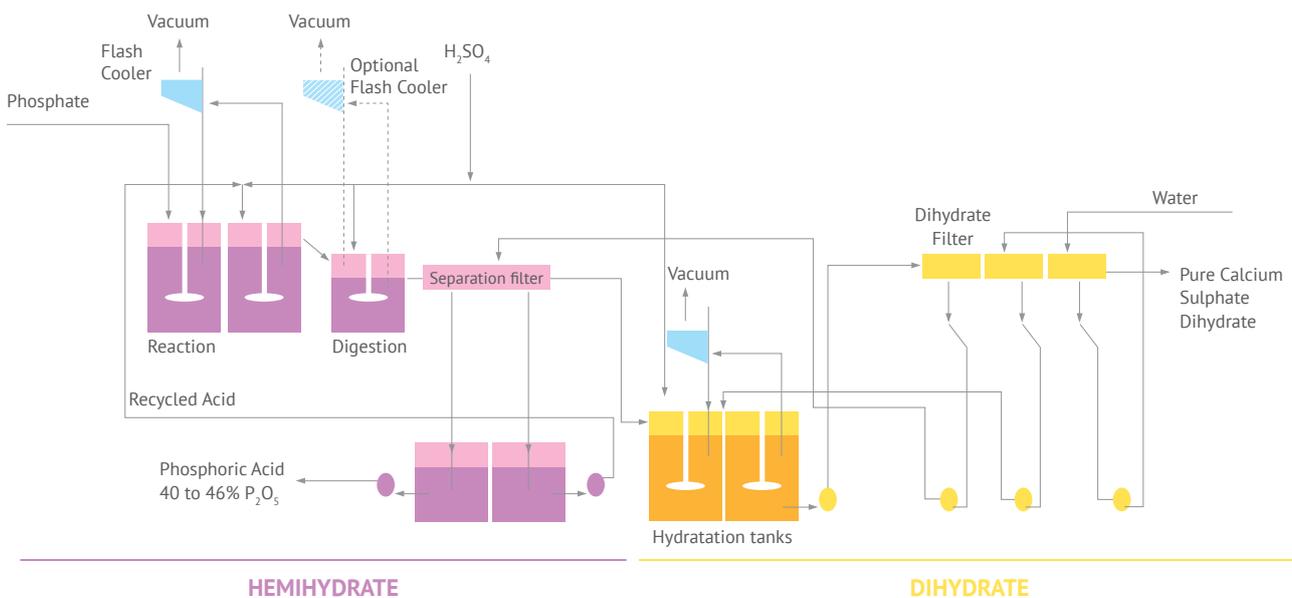
After the first reaction in hemihydrate mode, the product acid is separated as a 46% P_2O_5 with low SO_3 content. The remaining α -hemihydrate, washed with recycled liquor, is further processed with sulphuric acid in conditions in which α -hemihydrate is unstable and recrystallises as gypsum, releasing cocrystallised and unreacted P_2O_5 .

THE MAIN CHARACTERISTICS OF THE PROCESS ARE

- + high-strength phosacid
- + high P_2O_5 recovery (> 98.5%)

RECOMMENDED FOR LOCATIONS

- + with medium - high-cost rock
- + with high-cost energy
- + with easy gypsum disposal



ONE-CRYSTAL PROCESS OR PH1
[PRAYON HEMIHYDRATE 1-CRYSTAL]

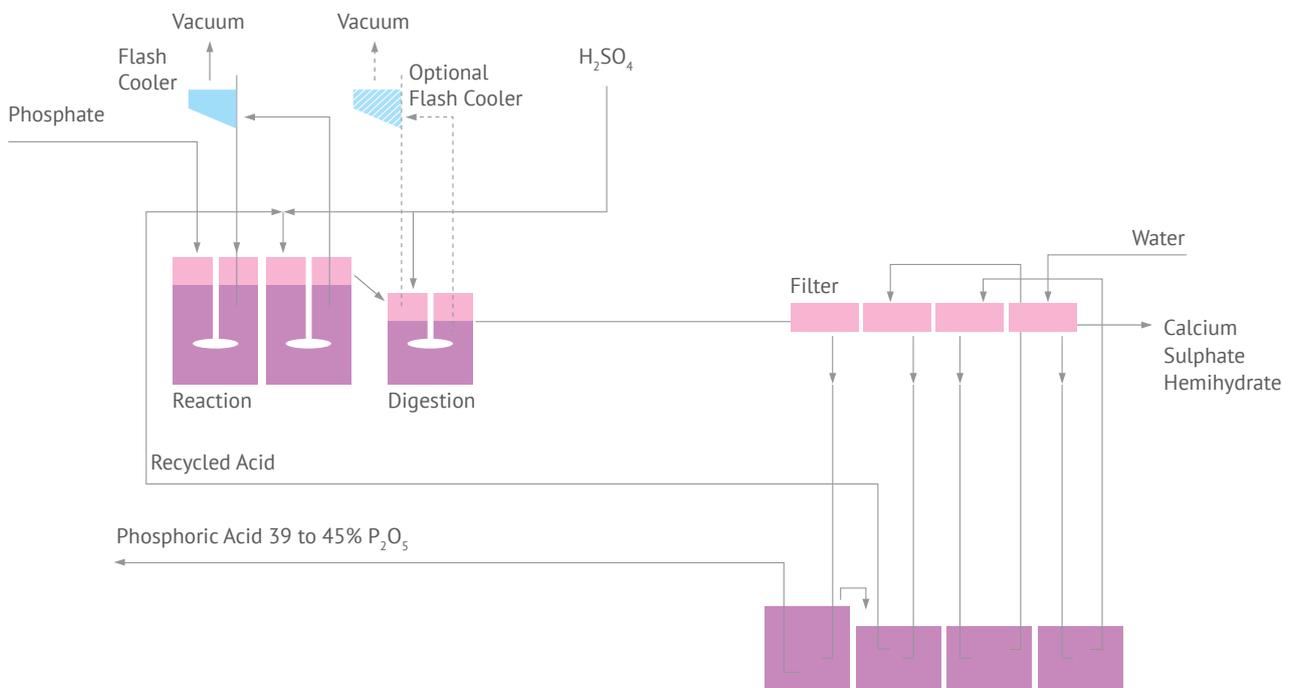
The reaction takes place in two stages. The first stage takes place with a low but positive sulphate level, while the second stage operates with a higher sulphate level. Perfect sulphate and temperature control permit the filtration of a slurry containing a highly stable hemihydrate with low scaling properties.

THE MAIN CHARACTERISTICS OF THE PROCESS ARE

- + simple and low-cost process
- + high-strength acid

RECOMMENDED FOR LOCATIONS

- + with low-cost rock
- + with low-cost sulphuric acid
- + with high-cost energy
- + where gypsum disposal is not a problem



HEMIHYDRATE

PRAYON RELATED TECHNOLOGIES

In order to improve the quality of the acid produced, PRT has developed numerous technologies to decrease the level of impurities and increase the P_2O_5 content of the product acid.

ACID CONCENTRATION

Designed to have an high efficiency and easy to operate.

FLUORINE RECOVERY

The specific equipment developed as well as the operation system ensures a very high absorption efficiency.

GYPSUM PURIFICATION

Gypsum purification step to produce a product that could be used in down-stream processes as cement plant.

ACID PURIFICATION

To improve product quality for specific applications.

- + Desulphation;
- + Cd removal;
- + As removal;
- + Defluoration;
- + MER reduction..;



CONCENTRATION AND FLUORINE
RECOVERY DROPLETS SEPARATOR

PROCESS LICENSING

- + Phosphoric acid production
- + Phosphoric acid concentration
- + Fluorine recovery
- + Gas scrubbing
- + Phosphoric acid treatment (F, As, S...)
- + Gypsum treatment
- + Uranium extraction from phosphoric acid

CONSULTING

If requested by the customer, Prayon Technologies can provide the following services:

- + Technical support for existing units
- + Training of operators
- + Phosphate rock evaluation
- + Agitation optimisation

Prayon
Technologies

PRAYON TECHNOLOGIES S.A.
LICENSING DIVISION OF PRAYON

Rue Joseph Wauters, 144
B-4480 Engis

Tel. +32 (0) 4 273 93 41
Fax. +32 (0) 4 275 09 09
mail. prt@prayon.com

www.prayon.com