# Prayon's Hemihydrate Technologies

## by


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### ABSTRACT

Although Prayon's licensing activities have during the past 10 years been principally based on the Dihydrate process for phosphoric acid production, their own production activities, based in Engis Belgium, are based on the two-stage Dihydrate Hemihydrate CENTRAL-PRAYON process. This high efficiency process, ± 98.5% cake efficiency, also now produces a relatively strong acid, ± 36% $P_2O_5$ .

In the late 1970's the oil price increased and this put pressure on PRAYON to develop higher strength processes and two alternatives were envisaged. Firstly to develop a process with the first stage as Hemihydrate to produce 48-52% $P_2O_5$ acid or secondly to modify the operating conditions of the existing CENTRAL-PRAYON plant to achieve a product acid strength higher than the 33-34% attained at that time. The eventual solution should produce a merchant grade gypsum with similar qualities to that obtained before for downstream use by the plaster manufacturer.

A single stage HH process could not achieve the quality of gypsum required by the downstream plaster producer nor a high enough efficiency to produce phosphoric acid economically at the inland European site. A two-stage Hemihydrate-Dihydrate process would have a higher efficiency but the drying step would be costly, the Hemihydrate has self-drying characteristics absorbing the free water during hydration.

A novel Hemi-Di-Hemi process was developed with two recrystallization stages and two filtration stages. This process was named the **PRAYON Hemihydrate 3-crystal** process, or **PH3**. This process could produce a 45% $P_2O_5$ acid with a 98.5% process efficiency and a high quality Calcium Sulphate.

During the development period the existing CENTRAL-PRAYON plant had managed, with the use of additives to reach 36-37% $P_2O_5$ with the production of an acceptable gypsum. Due to this success and the lowering of the crude oil price the **PH3** was not built at Engis.

For less stringent conditions; outside Prayon, where the gypsum quality is not so critical the deletion of the final stage of the **PH3** process leads to a Hemihydrate-Dihydrate process which is of more interest and as such was developed for licensing purposes, this was called the **Prayon Hemihydrate 2-crystal** process, or the **PH2**. This process can produce a 50% $P_2O_5$ acid and has a process efficiency of >98%.

Where lower efficiencies can be accepted deletion of the dihydrate stage creates a single-stage Hemihydrate process. This process was also developed and called the **PH11** this can produce acid up to 45% $P_2O_5$ whilst maintaining a process efficiency of around 95% depending on the phosphate and the grind. If lower strengths can be accepted the efficiency would be higher or alternatively higher strengths may be obtained sacrificing efficiency.

A completely novel process, called the **PH12,** is similar to the **PH11** but in this case a second stage is added. The product acid is taken off in a first filtration stage and then the insoluble $P_2O_5$ is leached from the hemihydrate cake in a second stage with higher free sulphuric acid, followed by rewashing in a second filtration stage to recover the released $P_2O_5$. This enables higher process efficiencies whilst maintaining the same acid strength as the **PH11.**

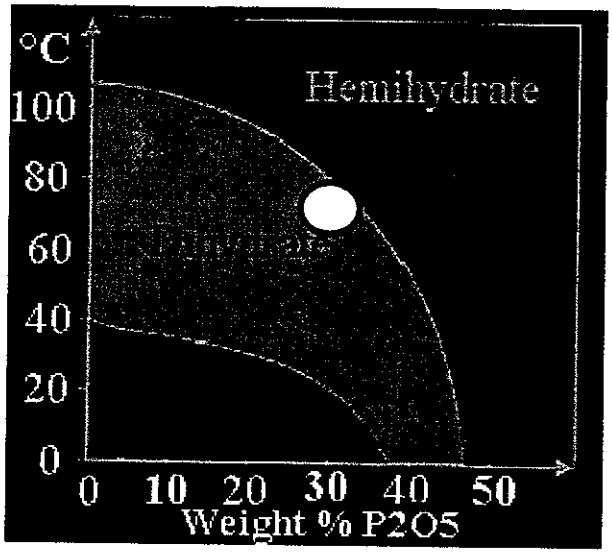
One of the main drawbacks linked to the high strength technologies used up to the present time has been the feeding of the HH filter with a high temperature slurry. This has caused problems with the resistance of filters and also from a scaling point of view. This scaling being principally in the form of fluosilicates. The Prayon processes differ from previous processes in that the reaction section is divided into two distinct zones. In the first zone high temperature & low sulphate give good dissolution conditions (high temperature and low sulphate), the parameters of the liquid phase of the slurry (high temperature) give it a high solubility maintaining the maximum of MCP/DCP in solution, and also conditions are favourable for the prevention of the formation of anhydrite (low sulphate). In the second zone the temperature is lowered, by a trim Low Level Flash Cooler (or air cooling on smaller units) and the sulphate is raised by the feeding of additional sulphuric acid. This creates the conditions for precipitation of the MCP/DCP in solution in the form of a highly filterable hemihydrate-$\alpha$ and the feeding of the filter with a solution having a much smaller quantity of dissolved fluosilicates due to the lower temperature.

Although the occasion to build plants to these **PH** technologies has so far not yet concretised, the features of the **Prayon** reactor and **Prayon** low level flash-cooler and the **Prayon** filter with its latest design of ***"fast-drain"*** pans are well known within existing dihydrate and hemihydrate units and with these building blocks and the specific features of the **PH** family of processes, developed based on "in-house" experience of hemihydrate operation with the CENTRAL-PRAYON process, both stand us in good stead for the design of perhaps the most reliable family of high strength processes in the world.

*Prayon's*
*Phosphoric Acid*
*Process*
*Portfolio*

*Development of DH Processes*

## *Phase diagram - $CaSO_4$*




## *Development of DH Processes*
## Dihydrate Prayon Process

- DPP **DH**

# Prayon's Aims

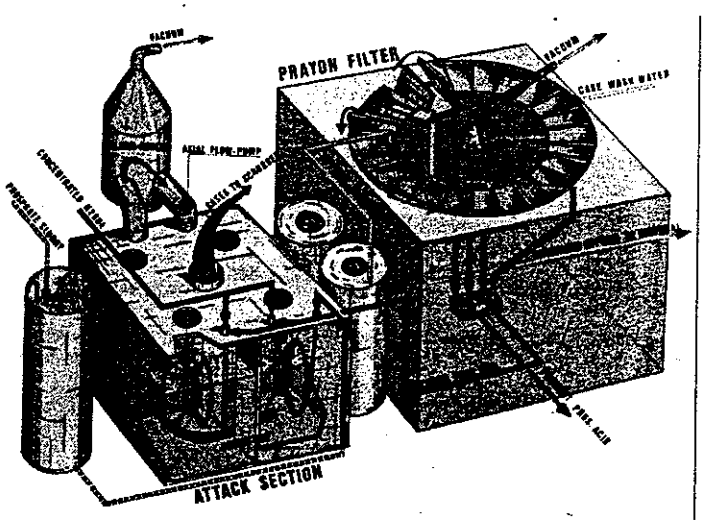
Building Blocks - Proven technology & equipment

**reliability**

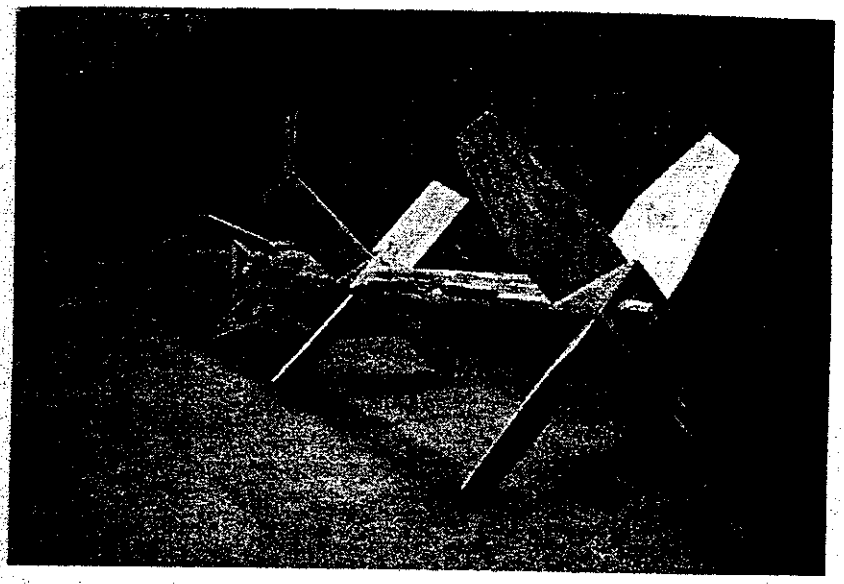
Process Characterised by its concern about

**operability**

# Mark 4 Dihydrate Process



***160 kW "PRAYON" Attack Agitator***
***5 ft dia. Radial , 6.4 ft dia Pitched , 7.4 ft dia 4- PHT Blades***



# *BIRD-Prayon filter in South Africa*

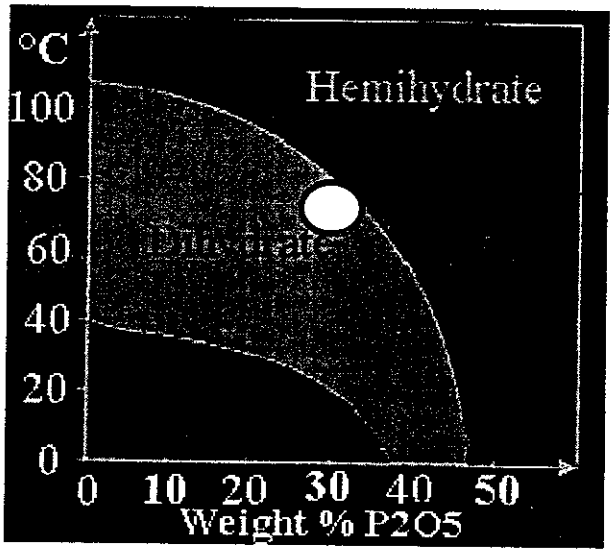
## *Technical Data after Upgrade*

- **Total filtering area 233,49 $m^2$ (+15.2%)**
- **Total useful area 199.44 $m^2$ (+16.5%)**
- **Possible useful area in wet discharge - 204.1 $m^2$ (cake discharge & cloth washing in one single hopper )**

## *Development of DH Processes*
## Central-Prayon Process

- DPP **DH**
- CPP **DH** **HH**

## *Phase diagram - $CaSO_4$*



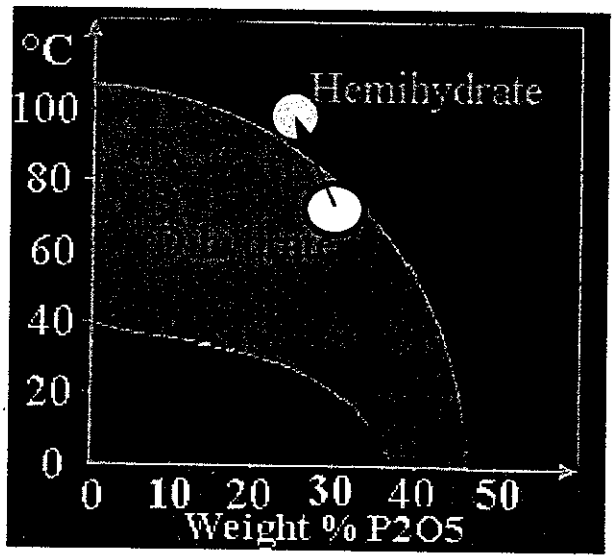

## Dihydrate Crystals

Process at **Prayon,** ENGIS, Belgium.

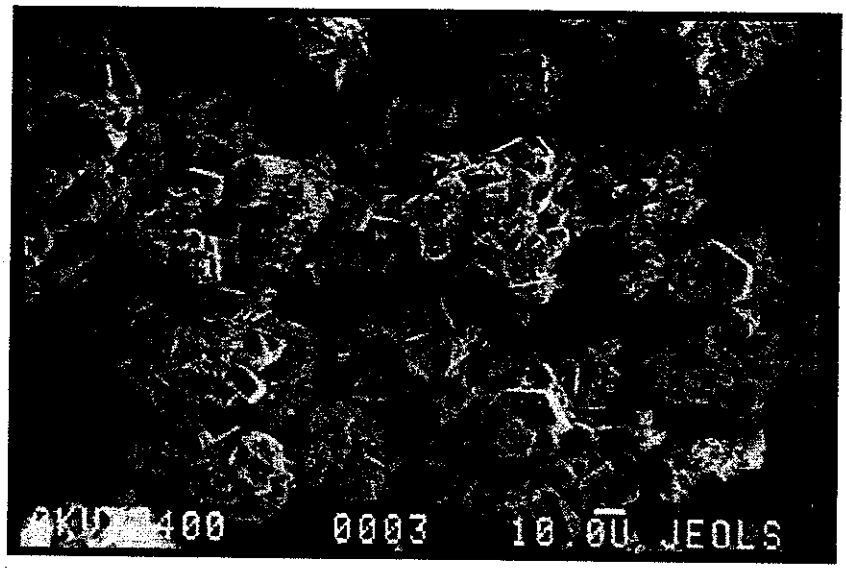
Central Prayon Process DH HH

1

## *Phase diagram - $CaSO_4$*



# Hemihydrate Crystals




2

Process at [redacted] ENGIS, Belgium.

Central Prayon Process DH HH

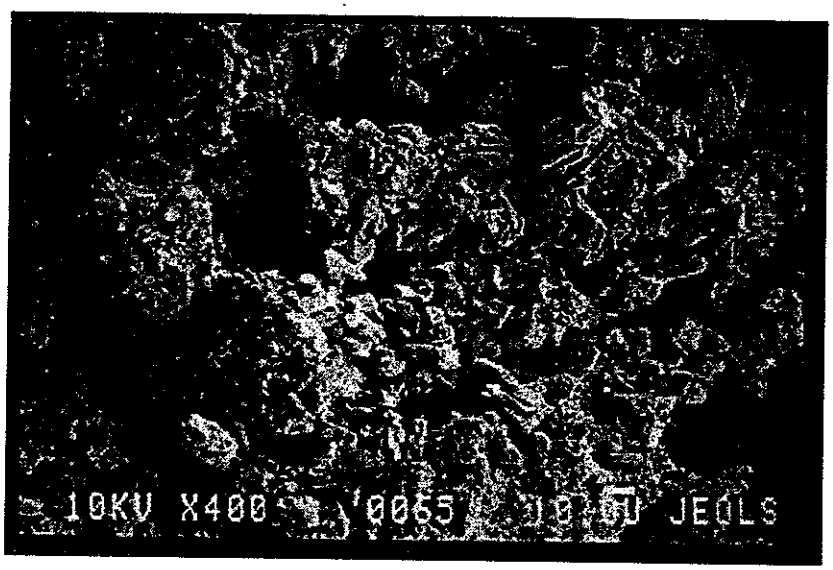
**Main features :-**

- High efficiency - Expensive phosphate
- Low sulfate, low fluorine acid - Less clean-up
- Higher strength - Less steam
- Good phosphogypsum - Sales + Low pollution
- Downstream plaster plant taking most of gypsum

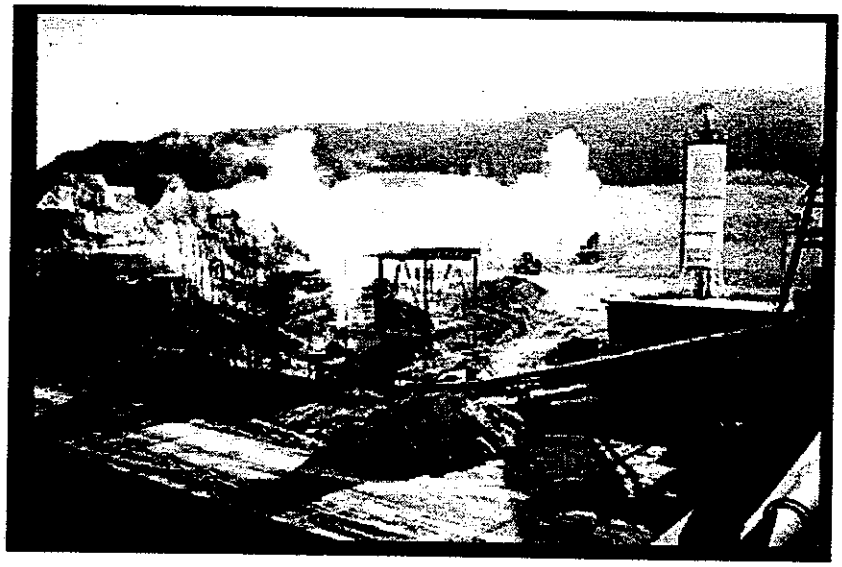
# Dry Disposal to Dry Stack

3

# Rehydrated Hemihydrate



## Feed to the Plaster Plant



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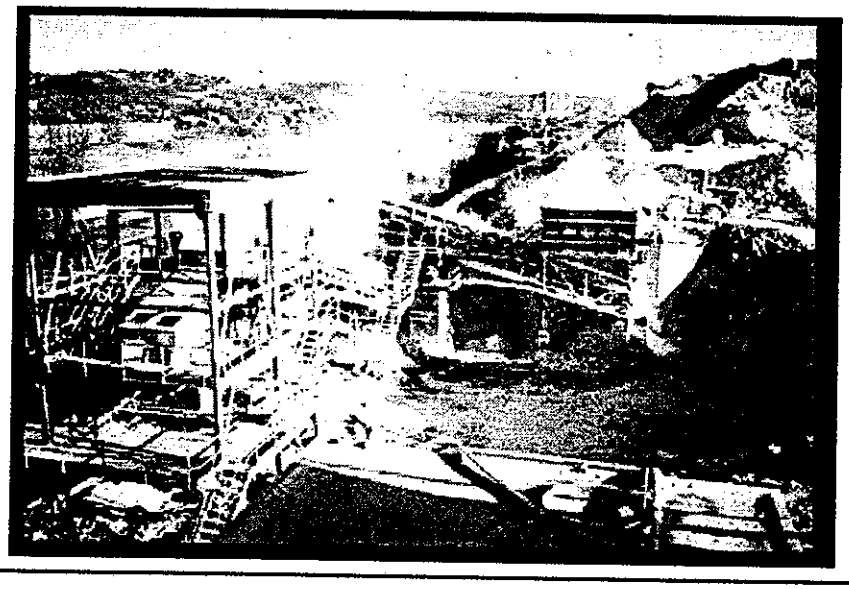
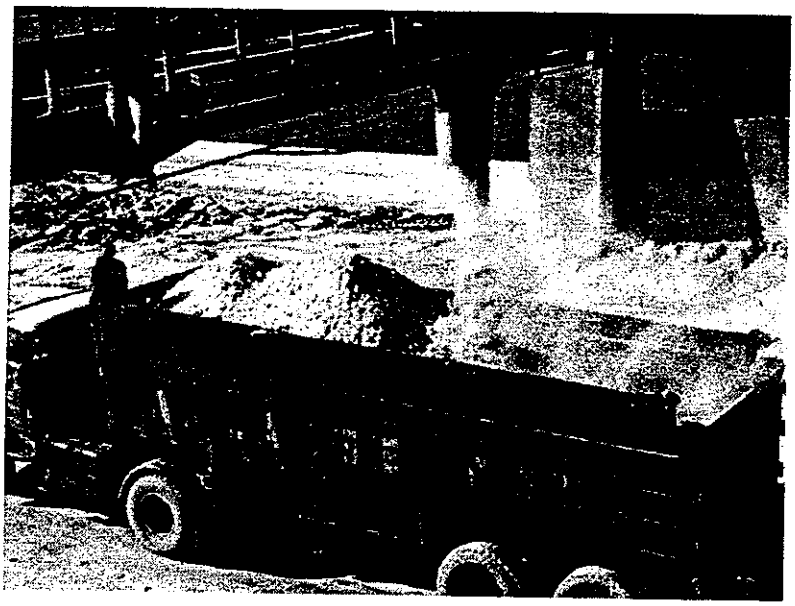
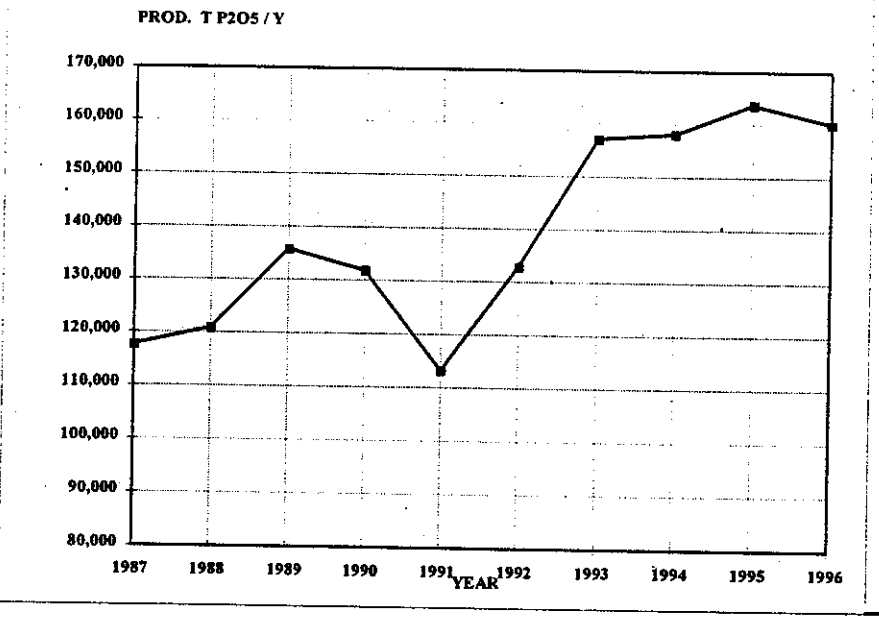


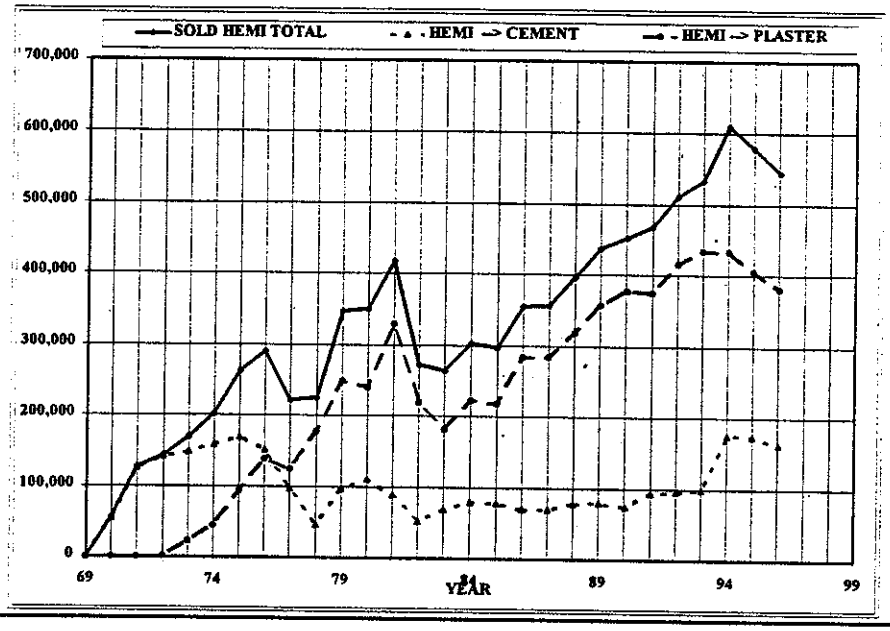
# Hemihydrate for Cement Retarder



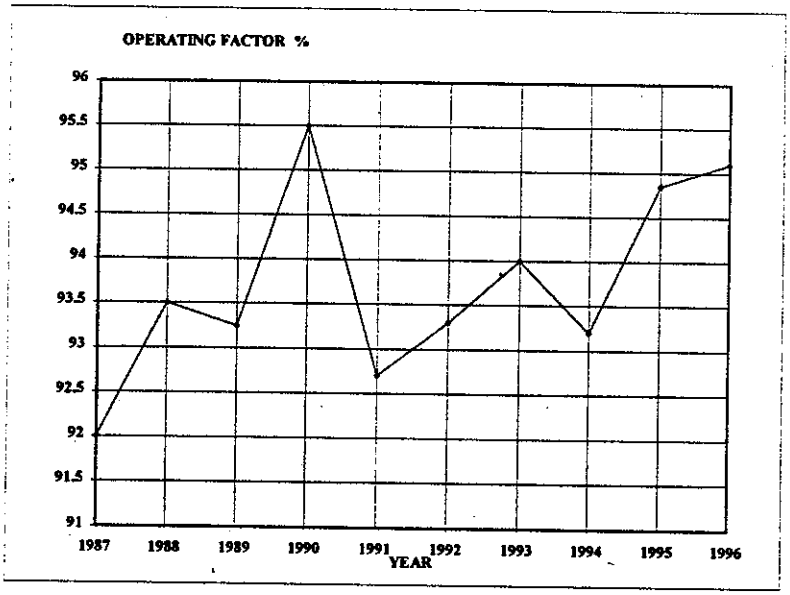
# Annual Production Rates



# Sales of Phospho-gypsum



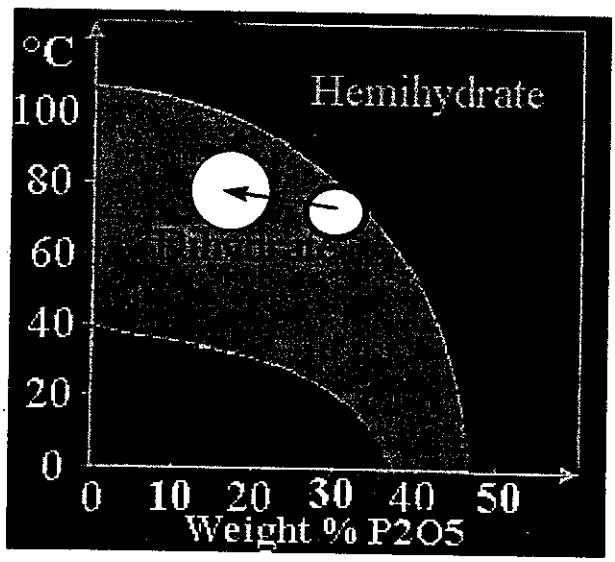

# Availability Data



## *Development of DH Processes*
## Double Dihydrate process

- DPP — DH
- CPP — DH — HH
- DDPP — DH — DH

## *Phase diagram - $CaSO_4$*



*Development of HH Processes*

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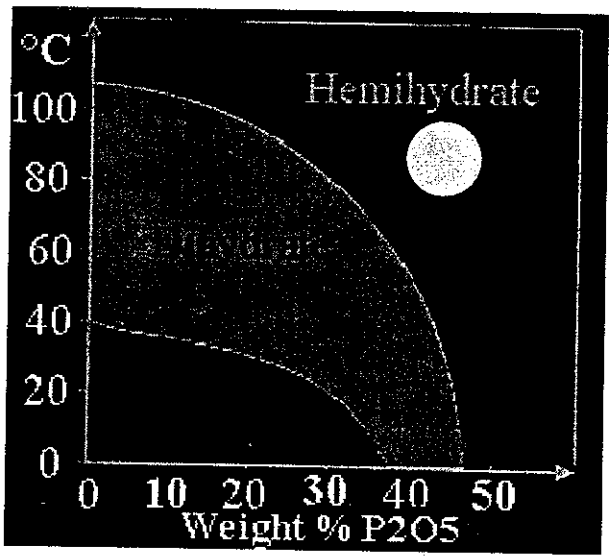


## *Development of HH Processes*

Limitations at **Prayon,** site, Engis

- Gypsum Quality - Downstream usage
- Gypsum Quality - Minimise pollution
- Gypsum Quality - Same spec. as before

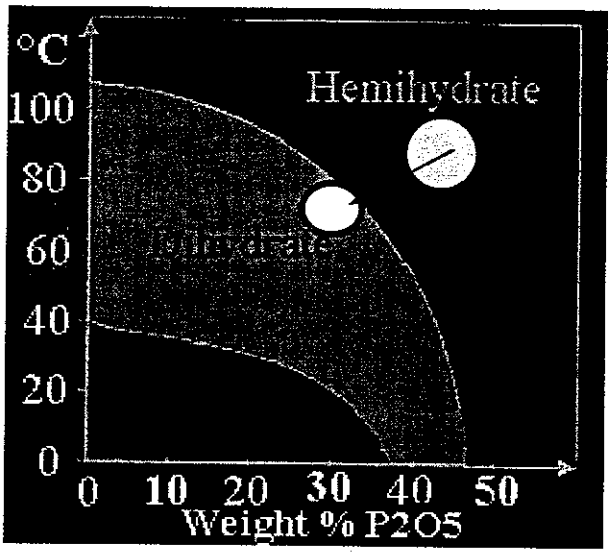
Process at **Prayon,** ENGIS, Belgium.

**Central Prayon Process** DH HH

PH3 HH + DH HH

**Prayon Hemihydrate 3-Crystal Process**

## *Phase diagram - $CaSO_4$*

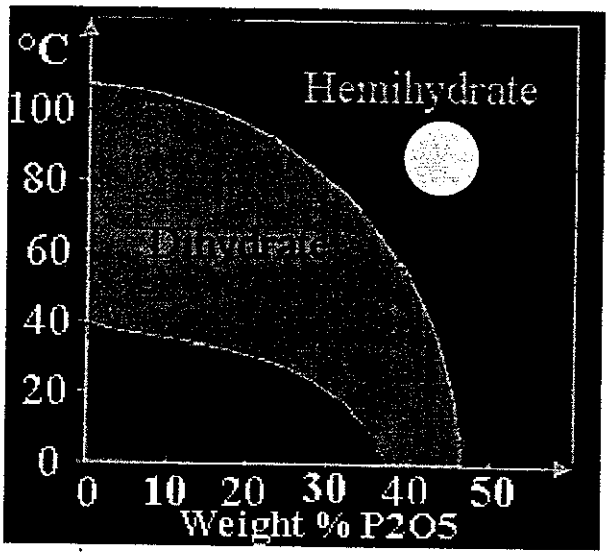



## *Development of HH Processes - PH11*

Prayon Hemihydrate 1 Crystal, 1 Stage Process

- PH3 — HH — DH — HH
- PH2 — HH — DH
- PH11 — HH

## *Phase diagram - $CaSO_4$*

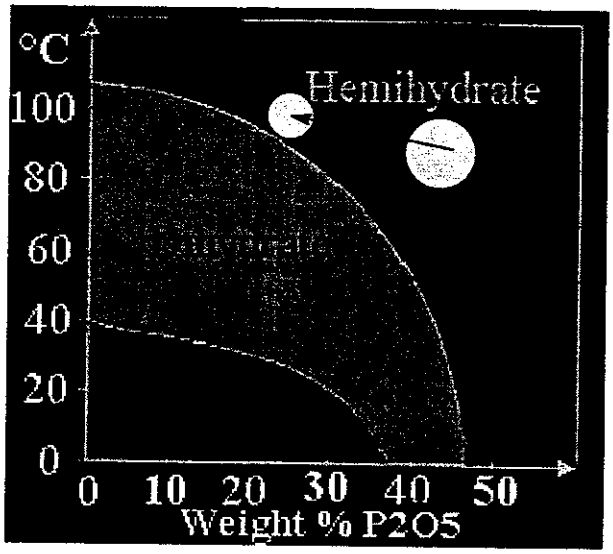



## *Development of HH Processes - PH12*

Prayon Hemihydrate 1 Crystal, 2 Stage Process

- PH3 — HH — DH — HH
- PH2 — HH — DH
- PH11 — HH
- PH12 — HH — HH

## *Phase diagram - $CaSO_4$*




## *HEMIHYDRATE PROCESSES*

A review as of 1997

## *Hemihydrate processes*

- **Single stage HH**
- Gyp, Hydro and PRAYON PH11

- **Two-stage DH-HH**
- Central-PRAYON

- **Two-stage HH-DH**
- Nissan "C", Hydro, PRAYON PH2

## *Single stage HH Processes*

- High strength
- Low efficiency
- Low cost
- Ease of operation
- Scaling

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- **Application :- Mine-site, where phosphate is cheap &/or utilities are scarce or expensive.**
- **Limitation :- Quantity of $P_2O_5$ in stack**

# *Two-stage processes*

Sites where phosphate is expensive

| | |
|---|---|
| * DH-HH | * HH-DH |
| * Central-Prayon | * PH2 or HDH |
| * 36% $P_2O_5$ | * 40-46% $P_2O_5$ |
| * **98.5% efficiency** | * **98.5% efficiency** |
| * small recrystallization vol. | * large recrystallisation vol. |
| * phosphate flexibility | * lack of phosphate flexibility |
| * **merchant grade gypsum** | |

## *Track records*

- **Single stage Hemihydrate**
- **Windmill Converted to HDH**
- **Hellenic Chemicals Shut-down**
- **Royster converted back to DH**

- **Two-stage Hemihydrate-Dihydrate**
- **Rikkihappo Oy Converted to Two Dihydrates**
- **Trepca Shut-down**
- **Albright & Wilson Shut-down**
- **Pivot Shut-down**
- **CSBP Shut down**
- **Supra Shut-down**
- **Copebras converted to Dihydrate**

## *Track records*

- **Two-stage Dihydrate-Hemihydrate**

  **11 units built, 4 still in operation**

- **Many small units in Japan & India shut-down**

- **Only process producing Merchant Grade Plaster, directly from filter**

- **Flexible as to the phosphate source, ease of conversion**

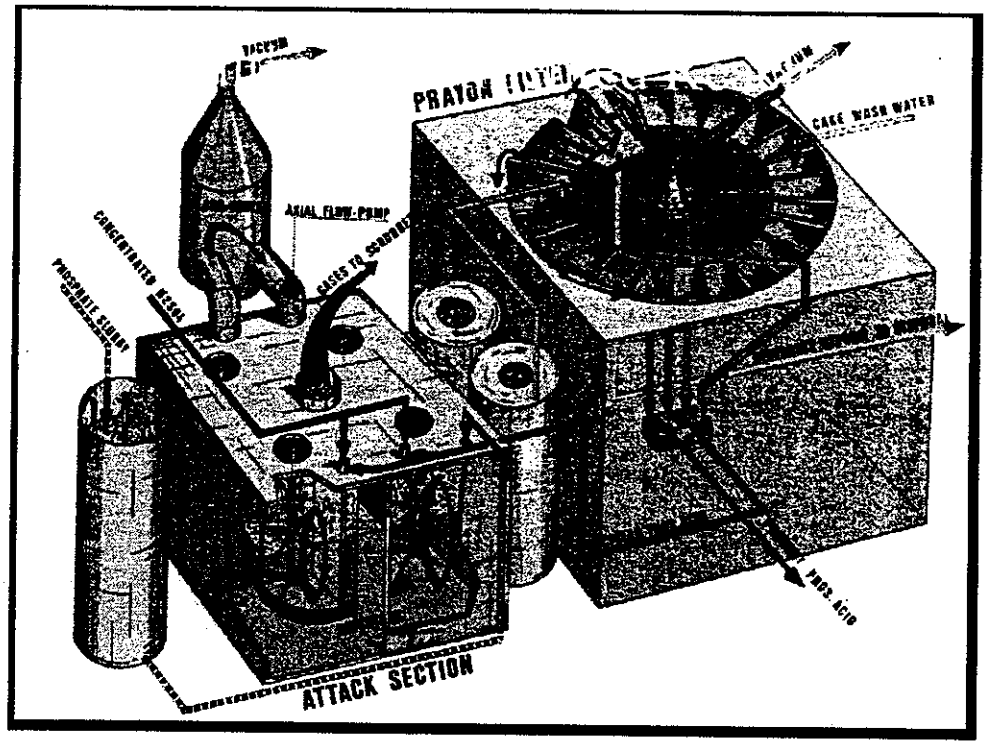
- **Selection of phosphate to make acceptable plaster**

- **Less limitations for use as cement retarder**

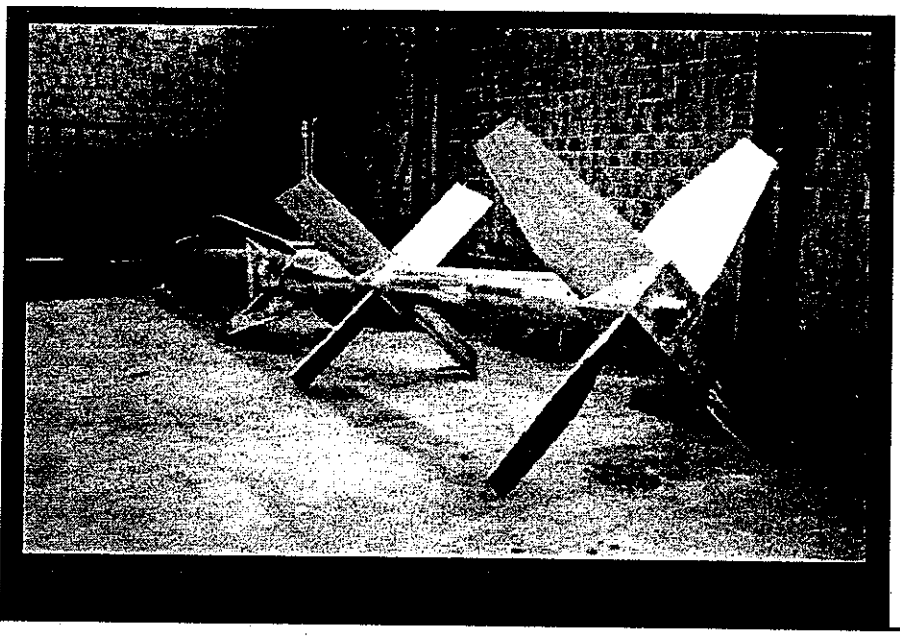
- **HH plants that ran the best**
- **Belledune and Arcadian**
  conversion of **PRAYON** plants built by **DAVY with mutli-compartment reactor & BIRD-Prayon *"Fast-drain" pans.***
- **Oxy**
  designed by **DAVY, some initial problems with foaming in the reactor & the UCEGO filter.**
- **Best running HH-DH plants**
- **NamHae**
  conversion of **PRAYON** plant built by **DAVY, with multi-compartment reactor but some initial problems with HH belt filters (2 x 90 $m^2$); DH filtration with BIRD-Prayon.**
- **Petrokemia**
  two **PRAYON** filters, now to be fitted with ***"Fast-drain" pans***.
- **Dong Bu**
  **PRAYON** filter with ***"fast-drain"*** pans used for Dihydrate.

# Prayon's capabilities for Hemihydrate

Building Blocks - Proven technology & equipment

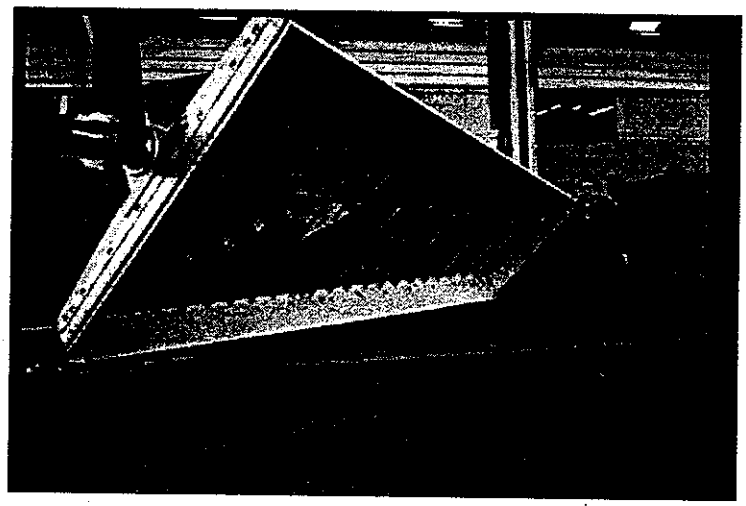



# Agitators



## *BIRD-Prayon filter fitted with "Fast-drain" Pans*

## A *"Fast-Drain"* Pan



# Prayon's capabilities for Hemihydrate

Building Blocks - Proven technology & equipment

[redacted]

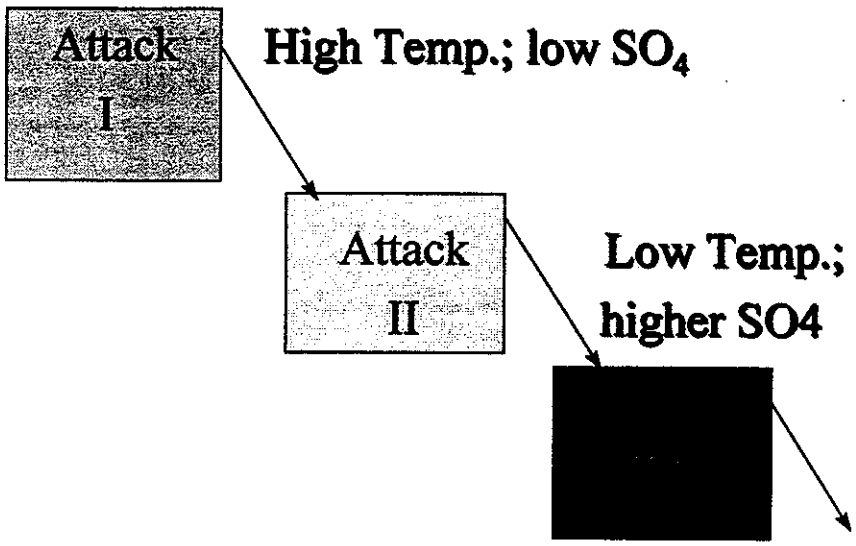
Process Characterised by its concern about

[redacted]

# PH processes characterized from other high-strength processes

- The reaction section is in two distinct zones
- The first zone high temperature, low $SO_4$ ; this prevents Anhydrite formation and gives good dissolution conditions and a high MCP/DCP solubility.
- The second zone is a lower temperature and a higher $SO_4$ level; this causes the precipitation of $CaSO_4$ in the Hemihydrate form, there is NO recirculation back to the first section.

## Block Flowsheet




## What are the results

- **Better crystal formation, less Anhydrite formation**
- **Lower temperature filter feed**
- **Rejection of silico-fluorides with the HH cake**
- **Greater rejection of $Al_2O_3$ with the HH cake**
- **Less scaling on the HH filter**
- **Lower corrosion rates on the filter**