Spring 2015

New Development in Dihydrate -Hemihydrate processes: The new Prayon DA-HF process

Tibaut Theys
Prayon

New Development in Dihydrate - Hemihydrate processes: The new Prayon DA-HF process

Contents

1. Introduction
2. CPP process
3. DA-HF process
4. DH plant conversion
5. Conclusion

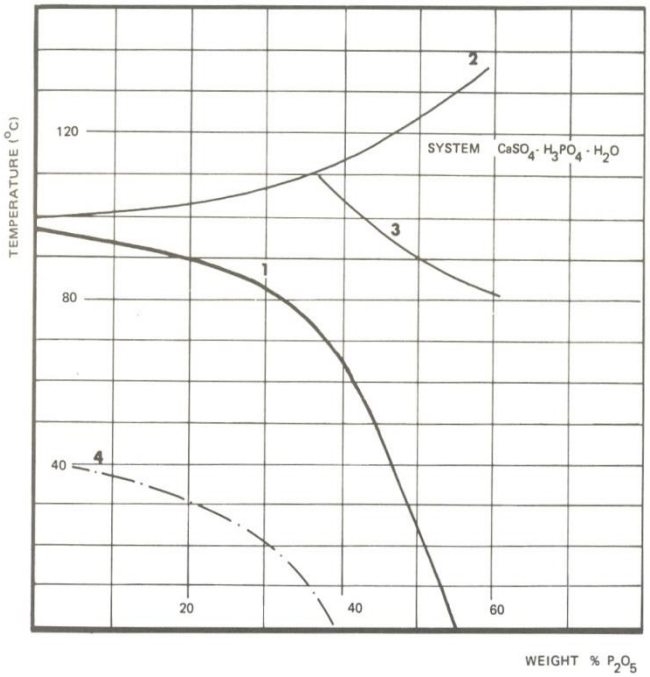
Introduction

$[Ca_3(PO_4)_2] + 3\ H_2SO_4 + x\ H_2O$

$3\ CaSO_4.2\ H_2O + 2\ H_3PO_4 + heat$

or

$3\ CaSO_4.1/2\ H_2O + 2\ H_3PO_4 + heat$



From P. Becker, Phosphates and phosphoric acid

Single Crystal	Double crystal Single filter	Double crystal Double filter
Dihydrate (DH)	Di attack – Hemi Filtration (DA-HF)	Dihydrate-Hemihydrate (CPP)
Hemihydrate (HH)	Hemi Re-Crystalisation (HRC)	Hemihydrate-Dihydrate (HH-DH)

New

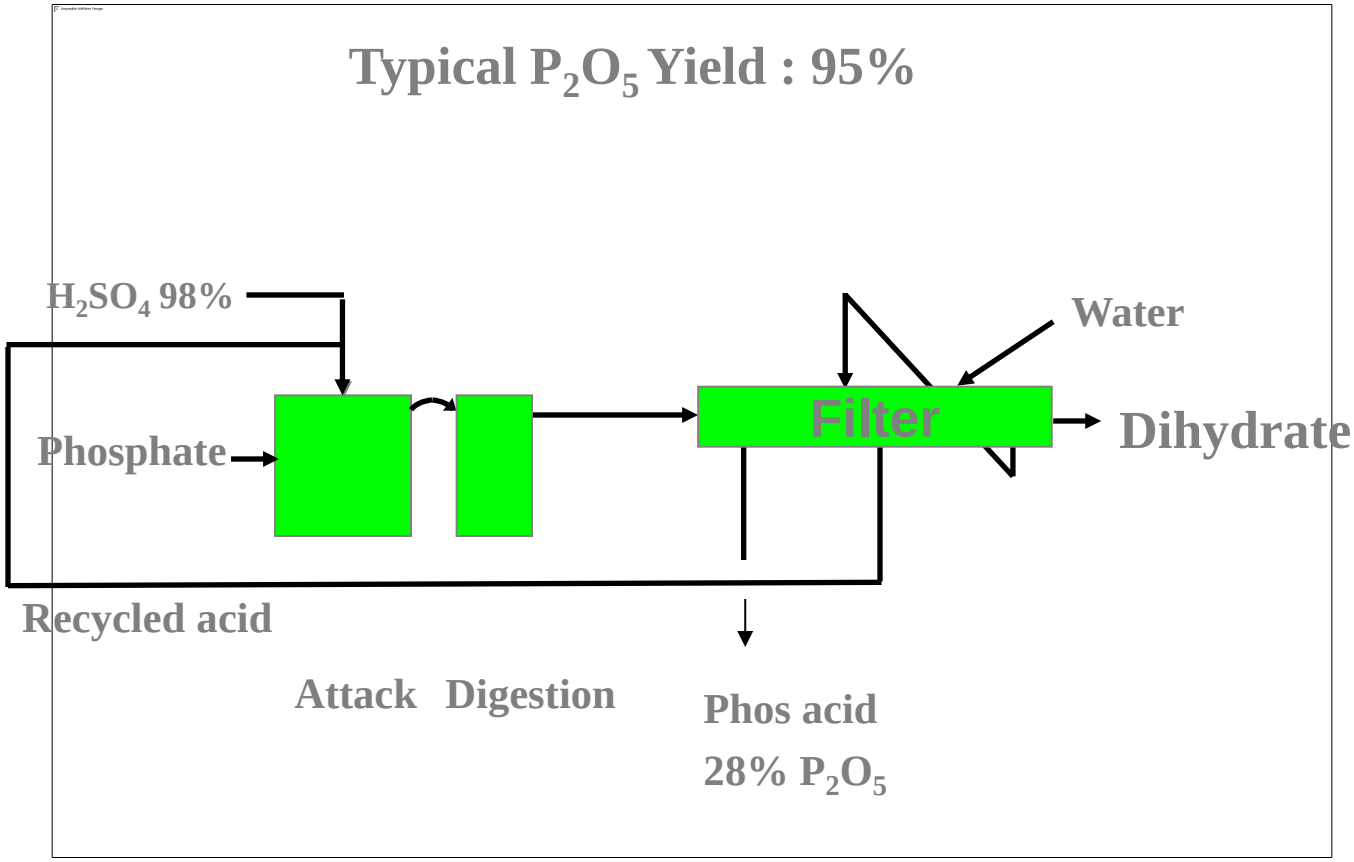
Introduction

- Plant revamping
  - Double crystal processes considered
  - Profitability limited by investment level
    - Extra filtration;
    - Extra conversion / crystallisation
- Prayon invests in R&D to improve plant efficiency and profitability
- One high newcomer: DA-HF process

From DH to CPP process

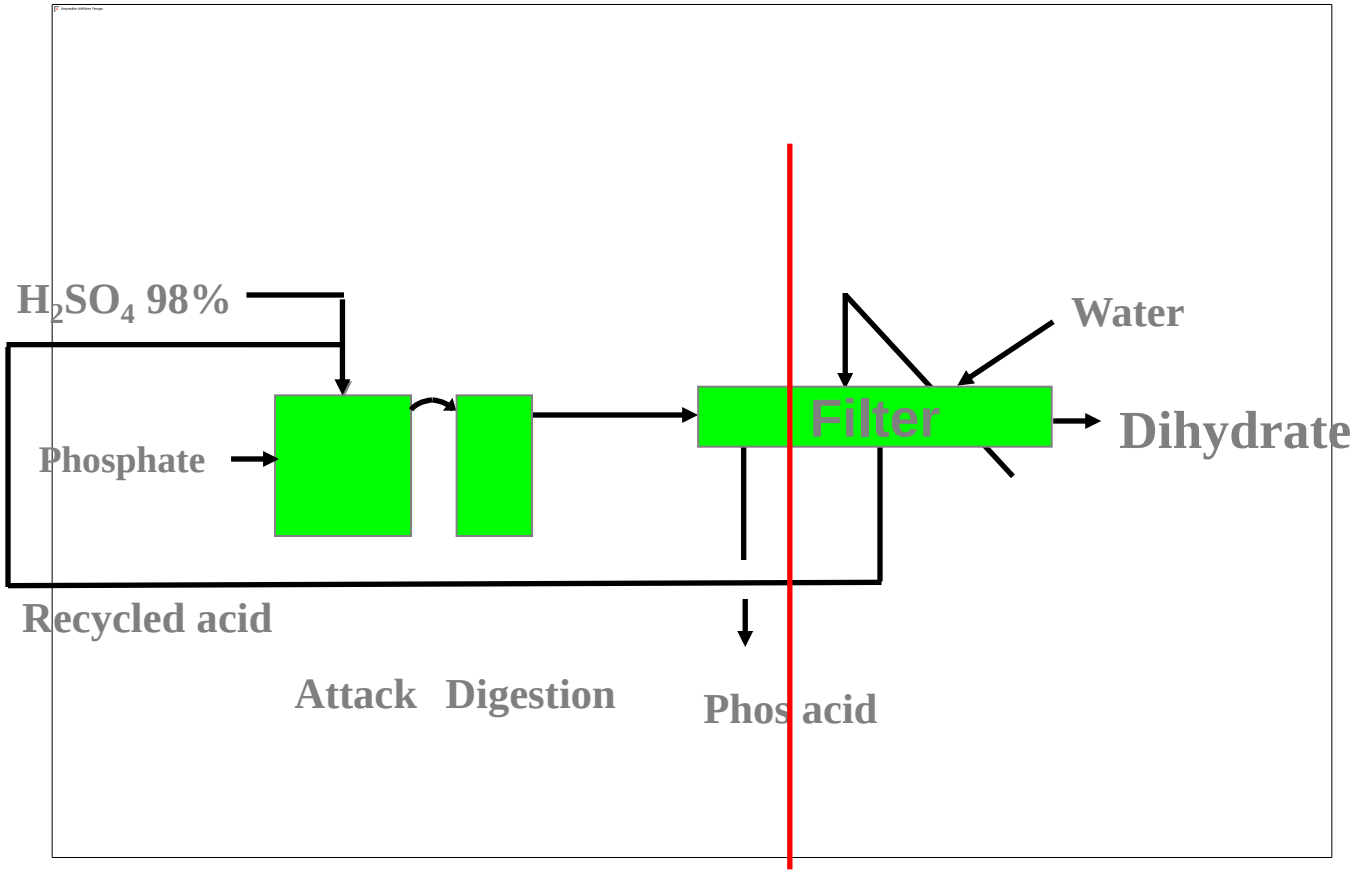
- 40 years ago
- Double crystal process
  - Gypsum seallable
- Stacking issue solved
- 90% of gypsum sold

Dihydrate Process

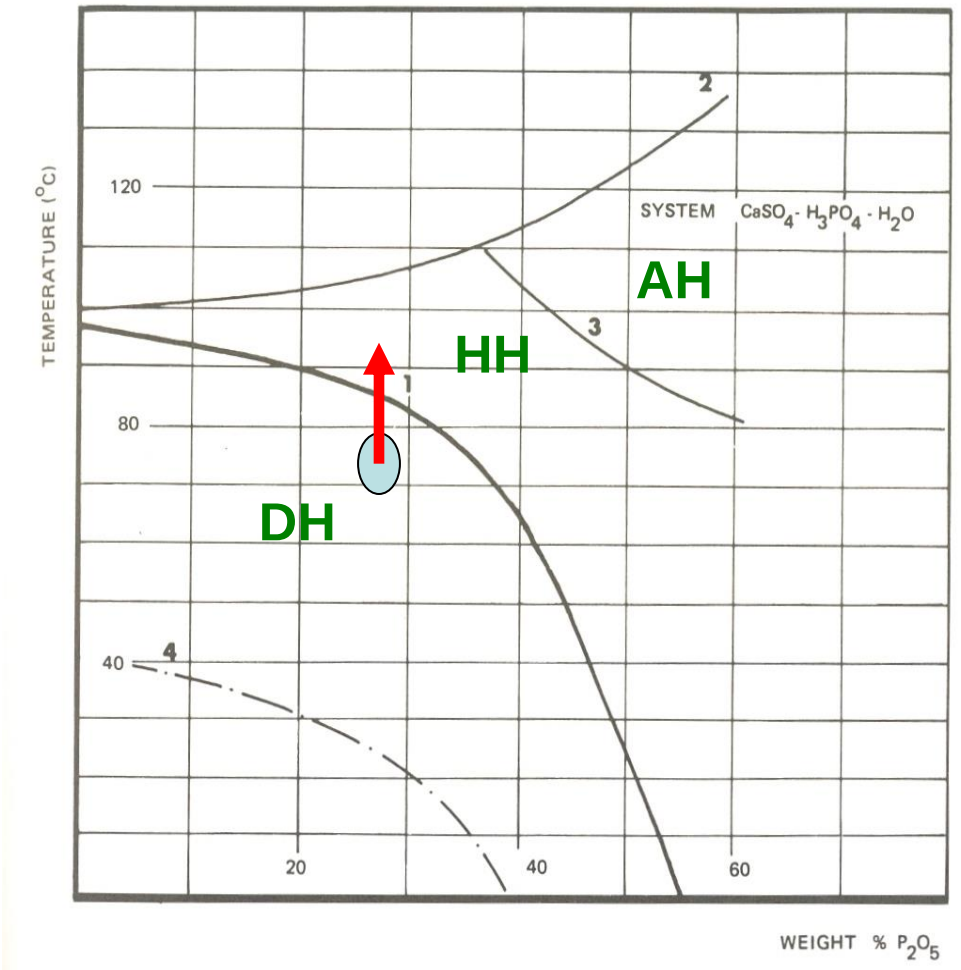


- Typical
- 28% P_2O_5
- 2,5% SO_3

Dihydrate Process

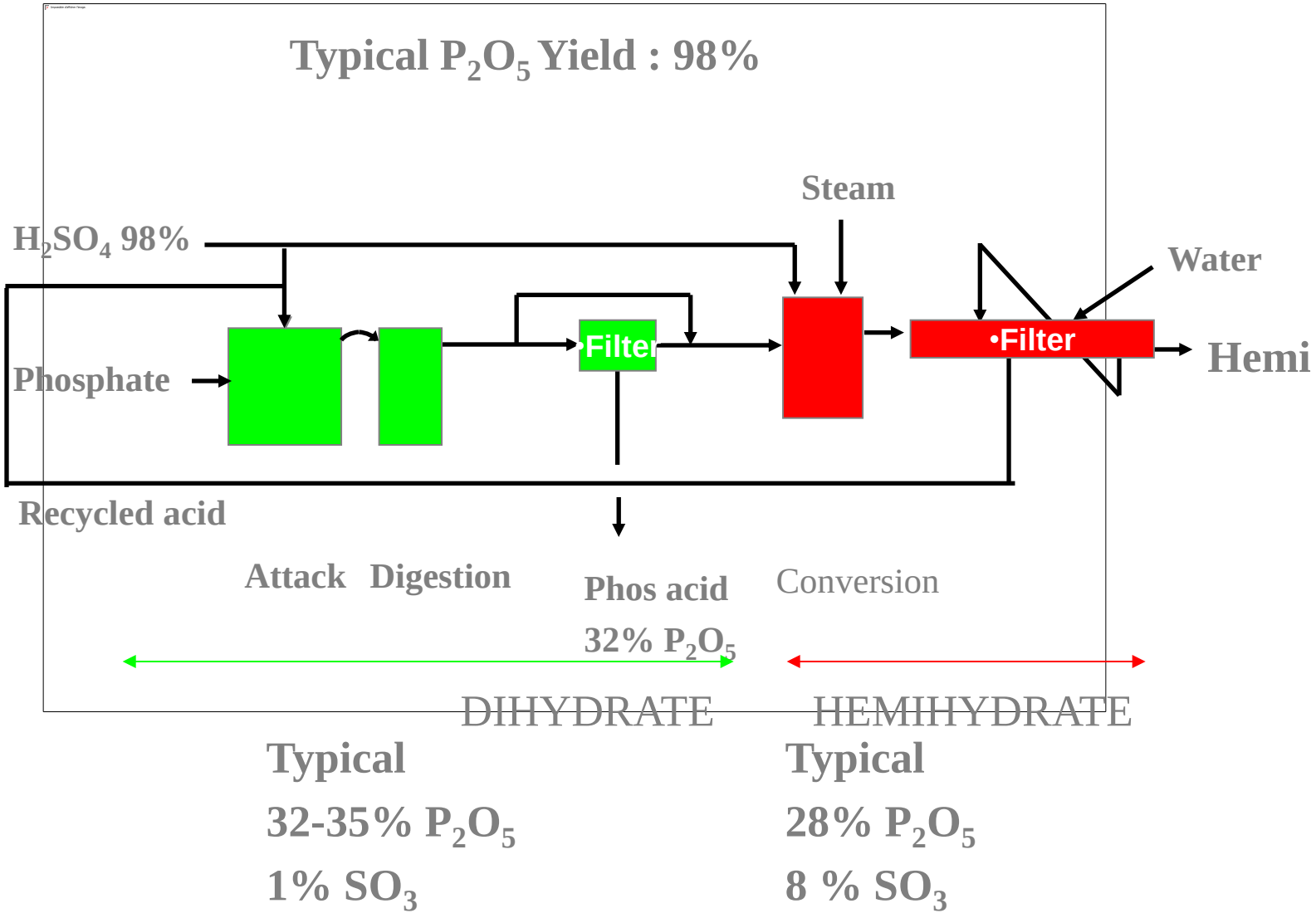


Stability regions of $CaSO_4$ hydrates



From P. Becker, Phosphates and phosphoric acid

Central-Prayon Process



PRAYON

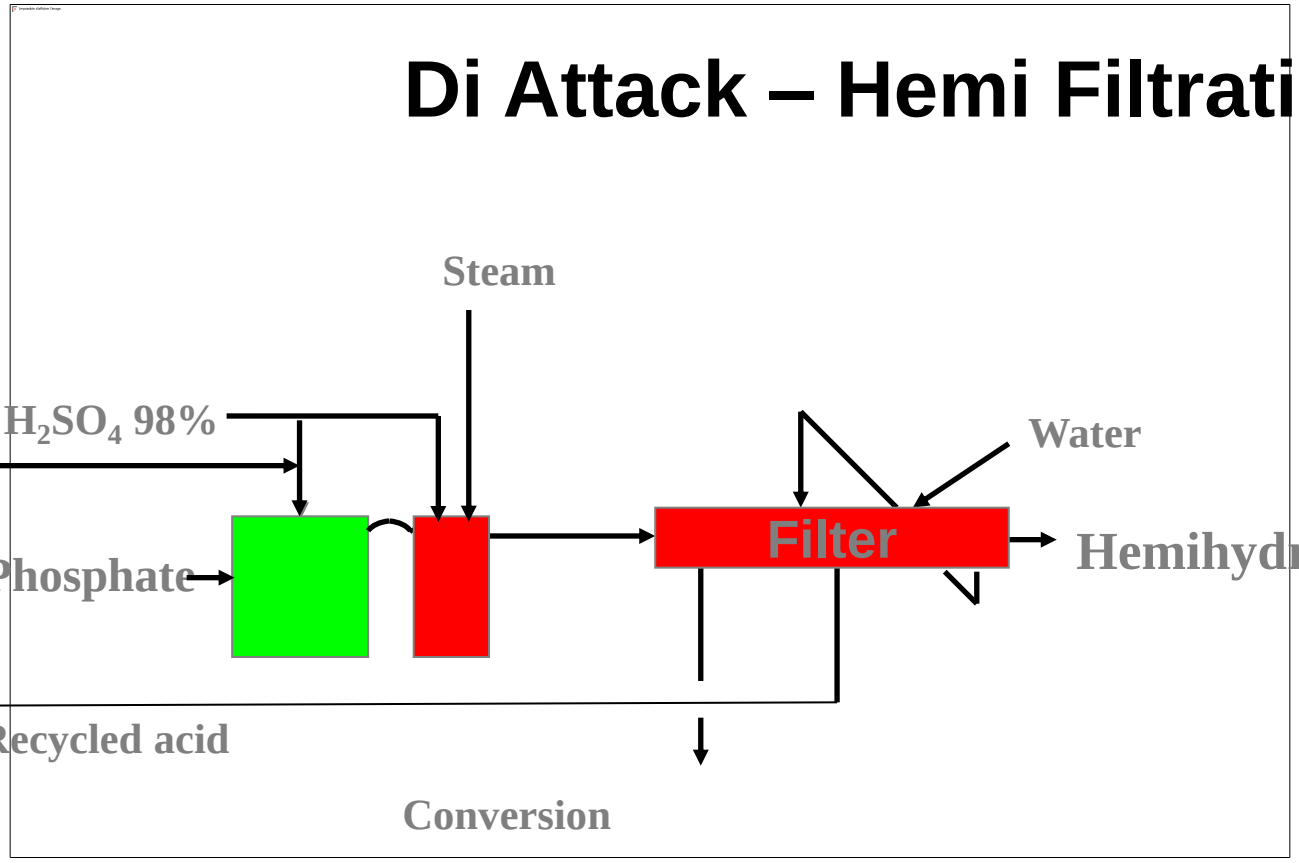
- **Advantages with respect to DH**

- **P2O5 Recovery higher than 98%**
- **Acid strength 32% P_2O_5 or higher**
- **Dry gypsum obtained after rehydration**

- **Disadvantages with respect to DH**

- **Higher capital cost (extra filter and conversion tank)**
- **More complex operation**
- **Somewhat higher maintenance costs**

Looking for a New Process route:



Di Attack

Hemi Filtration

28% P_2O_5

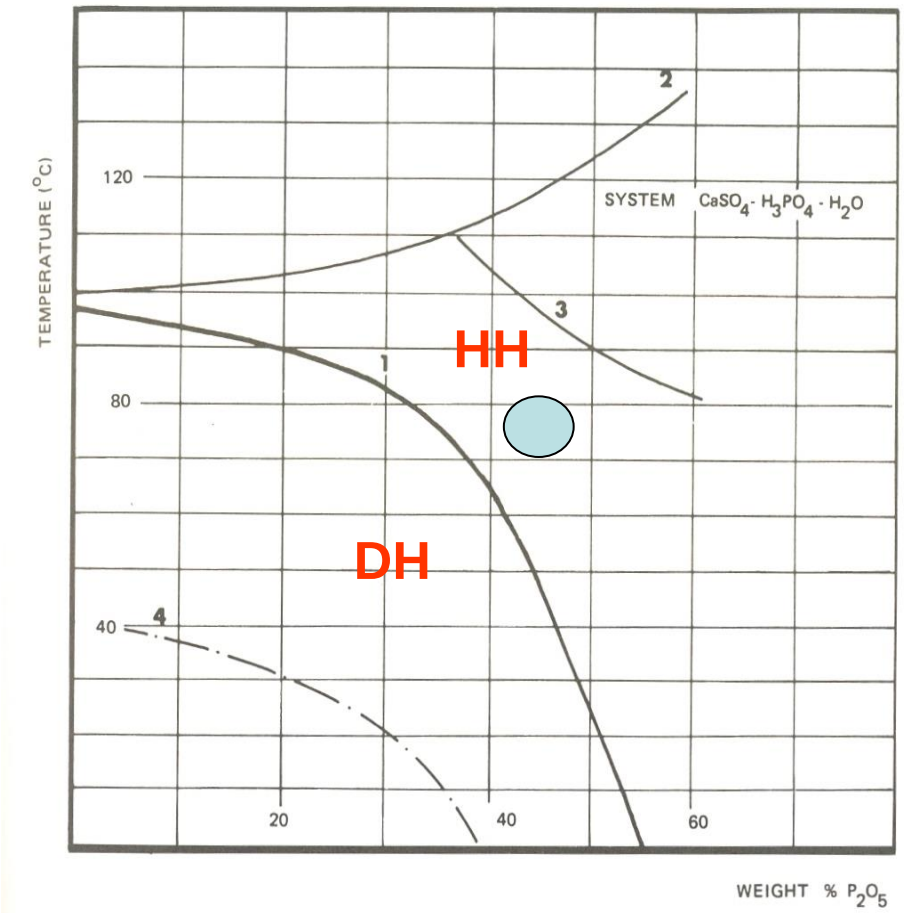
8% SO_3

Hemi Filtration

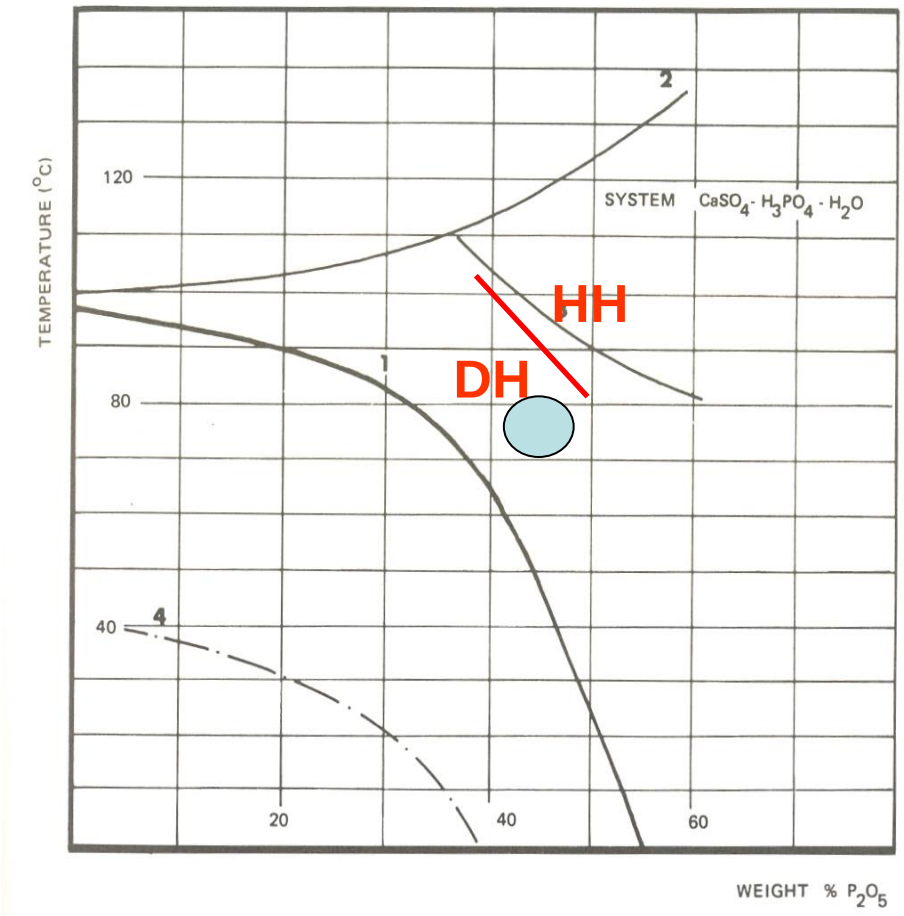
32-36 % P_2O_5

3% SO_3

The DH –HH conversion limits

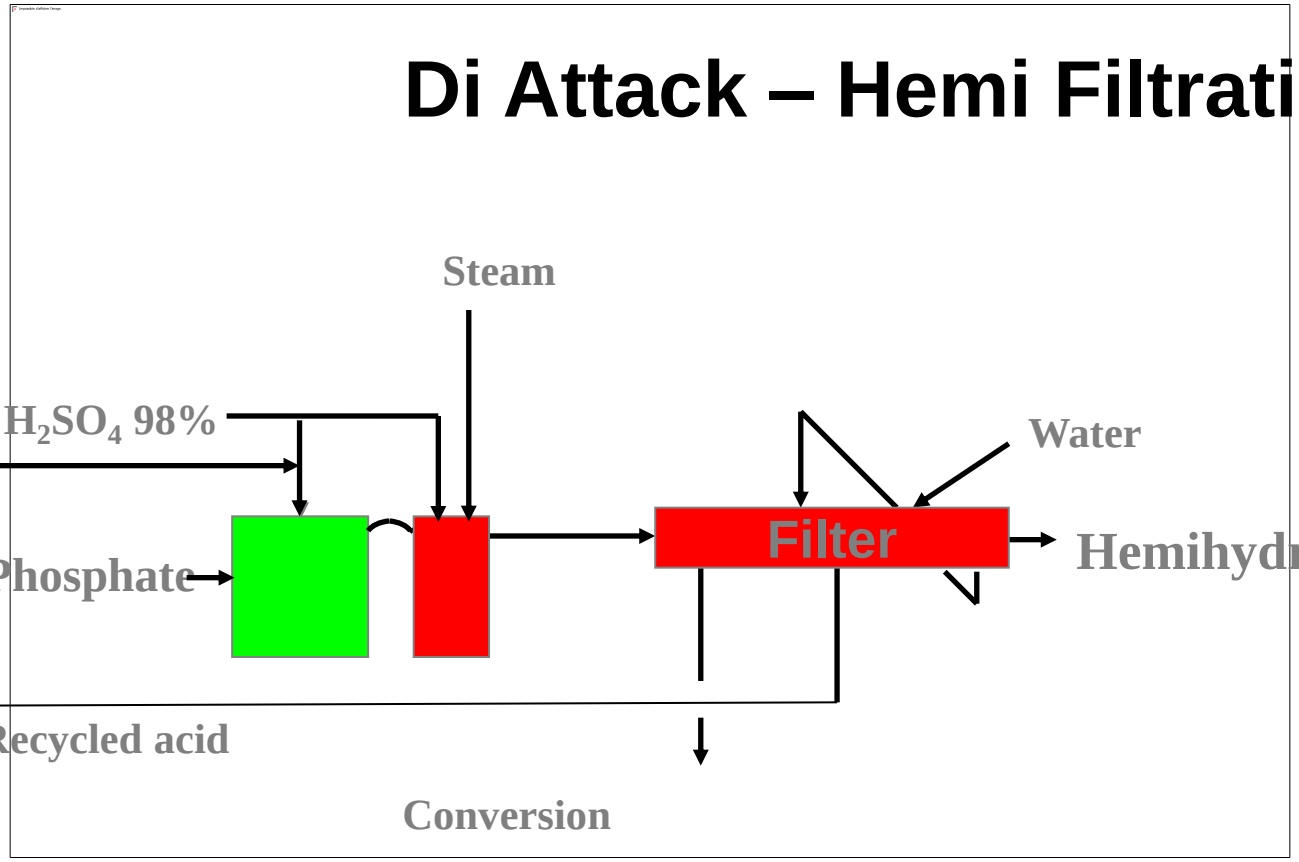


The DH –HH conversion limits



At very low sulfate content (0.2-0.4% sulphate)

Looking for a New Process route:



Di Attack	Hemi Filtration	Hemi Filtration
>37 % P_2O_5	28% P_2O_5 →	32-36 % P_2O_5
<0.8% SO_3	8% SO_3	3% SO_3

Pilot tests

Several rocks tested successfully

- Morocco, Syrian, Jordan, Kola, Egypt…

e.g. Syrian rock

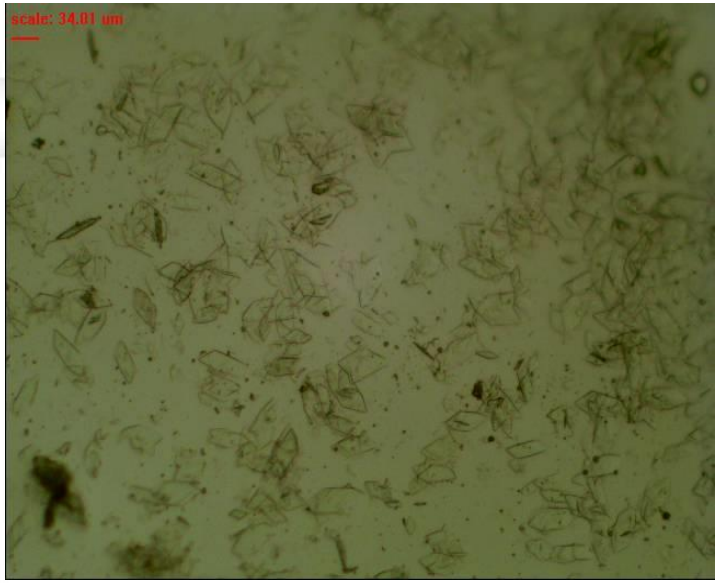
Rock analyses

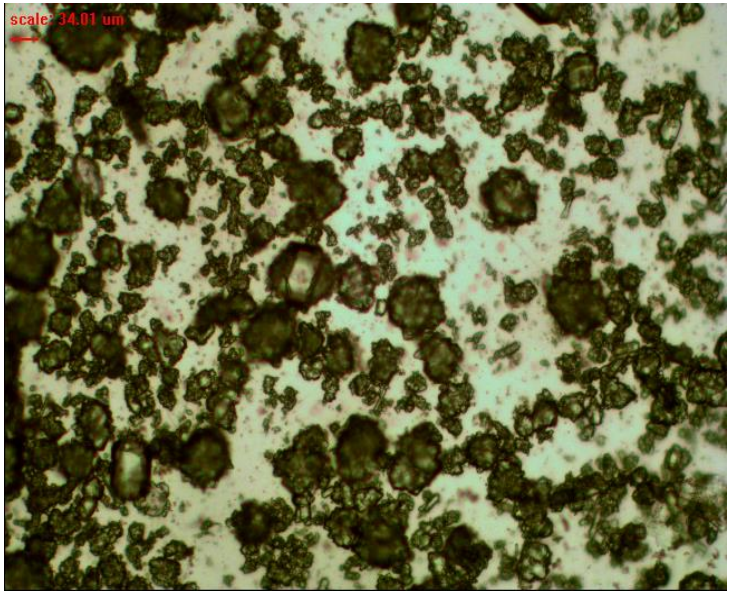
28,3 % P_2O_5,
47,9 % CaO,
3 % F,
6,8 % CO_2,

Pilot test with Syrian rock

Elements	Unit	Phosphate Rock	Gypsum (250°C basis)	Acid C2	Hémihydrate (250°C basis)
P2O5T	% w/w	28,3		36,08	0,2
P2O5UN	% w/w		0,07		0,11
P2O5 CO	% w/w		1,57		0,09
% SO3	% w/w			3,5	
Crystal water	% w/w		19,60		6,23
Efficiency	%				99%
Filtrability	tpdP2O5/ m^2 (cycle 180s)				5,99

PRAYON





For these conditions:

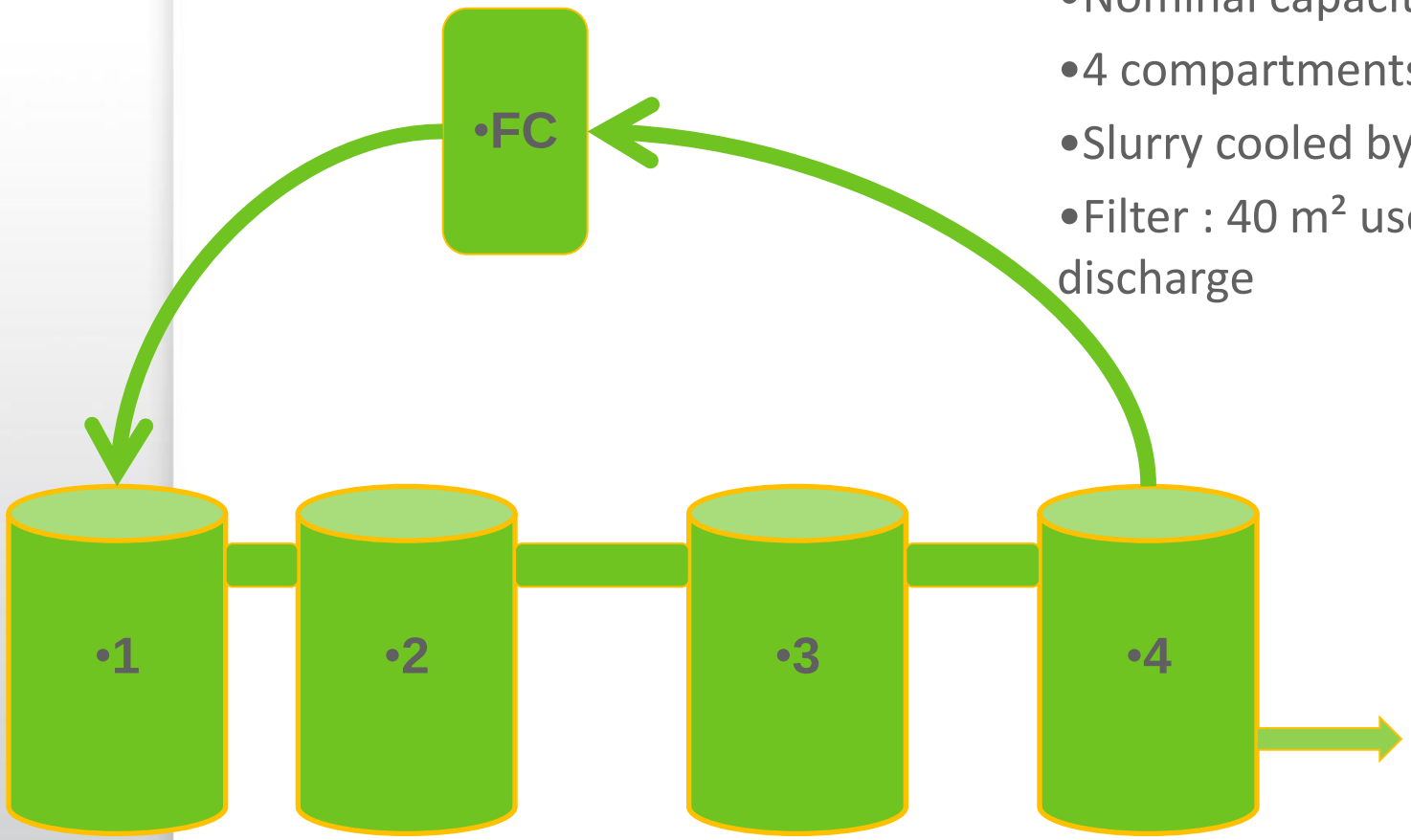
the P_2O_5 process recovery is > 2% higher than DH

the filtration rate is about 20% - 30% better than DH

Industrial Test Design

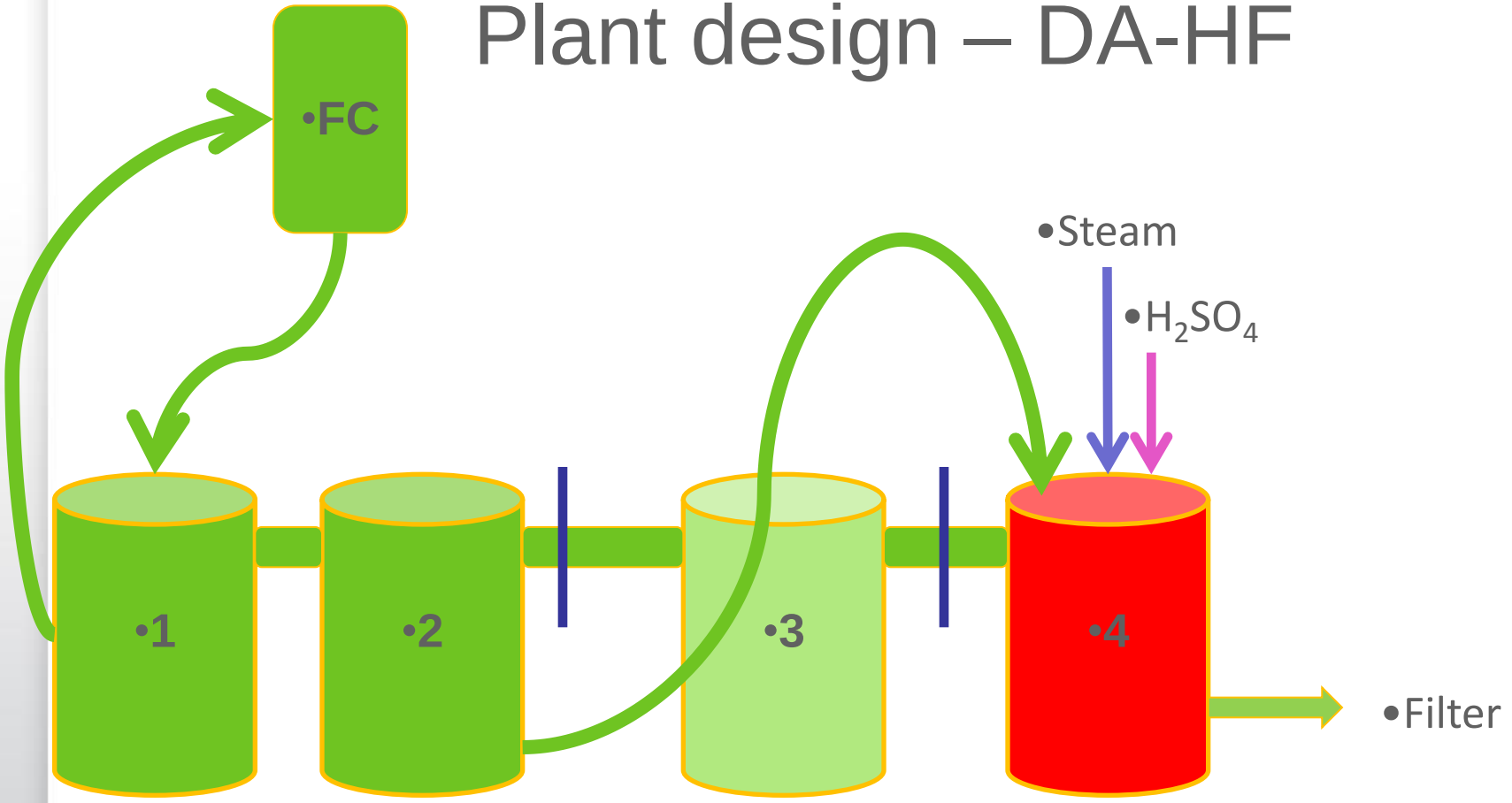
Plant design - Dihydrate

- Nominal capacity: 150 tpd P_2O_5
- 4 compartments 225 m^3
- Slurry cooled by flash cooler
- Filter : 40 m^2 useful – dry discharge



Industrial Test Design

Plant design – DA-HF



Test Results

- Quality of acid and gypsum
- Calcium sulphate filterability
- Efficiency
- Plant operation

Test Results - Analyses with Moroccan Rock

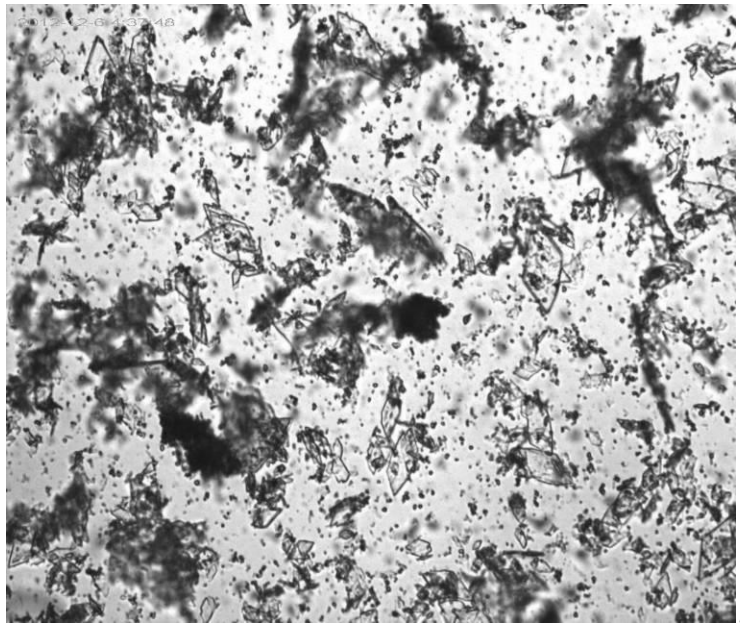
Elements	Unit	Rock Morocco	Acid DH	Gypsum (250°C basis)	Acid HH	Hemihydrate (250°C basis)
P_2O_5 WS	% w/w	30.7	37.4		32.85	0.2
P_2O_5UN	% w/w			1.42		0.11
P_2O_5 CO	% w/w			0.59		0.32
Crystal water	% w/w			19.60		6.3

Test Results - Filterability

		DH operation first test	DA-HF operation Morocco rock
Conversion			
Slurry temperature	°C	*76*	95
Filtrate Density	20°C	*1.308*	1.460
Filtration rate :			
Atm. Pressure (local)	(mmHg)	*760*	760
Filter Vacuum	(mmHg)	*500*	500
Filtration cycle	(s)	*180*	180
Filtration rate	(TPD P_2O_5/m^2)	*3.8*	5.4

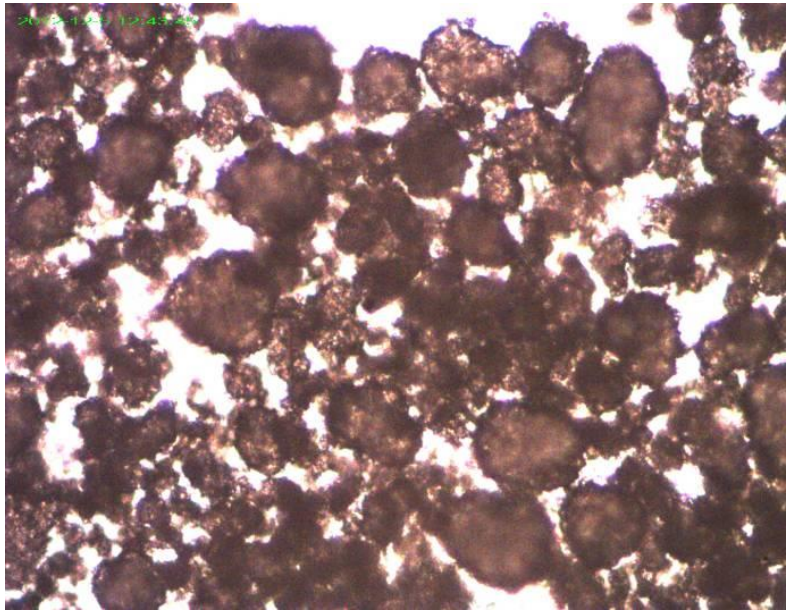
Test Results – DH Crystals

- Small individual crystals
- No clusters
- Slurry easy to pump



Test Results – HH Crystals

- Clusters
- Ball shape
- Aggregates easy to filter



Test Results – Efficiency

- Industrial values observed: 97 – 98%
- To be compared with a DH process results : 94-95%

Test Results – Plant Operations

- Some difficulties due to filter hopper not designed for HH operation (solids accumulation)
- Operators could easily operate the plant
- Start-up and shut downs are as easy as for DH process
- Flash cooler to be operated at lower pressure

Lessons learned for conversion of existing DH plant

	Check	Modify
Attack tank	Agitators, Cooling	
Digestion tank	Agitator, lining SA pipe	Steam injector New tank
Filter	Barometric legs	prewash Sectors
Cake discharge	Hopper Conveying	
Gas scrubber	capacity	

Most DH plants can be converted to DA-HF technology

Profitability – preliminary study

- Profitability highly linked to local condition
  - Energy cost;
  - Utility cost;
  - Usage of gypsum;
  - Raw material cost.
- For a new plant producing MGA (500 tpd P_2O_5)
  - Investment cost similar
  - Lower steam, P_2O_5 consumption
  - Profitability 7 to 25% higher
- For a revamping (500 tpd P_2O_5)
  - Without capacity increase : 2 to 5 years depending local conditions (Raw mat and reagents prices; selling of gypsum…);
  - With capacity increase: payback of less than 2 years.

Concluding remarks

With the all the challenges ahead (raw materials, energy, environment) phosphoric acid production remains an exciting field for process developments

Thank you for your attention !

Contact:
Tibaut THEYS
Tel: +32.4.273.93.41
Fax: +32.4.275.09.09
prt@prayon.be