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Latest Trend for Fluorine in the Phosphoric Industry: Absorption Efficiency Improvement, Conversion into Raw Material

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Latest trend for fluorine in the phosphoric industry: Absorption efficiency improvement, conversion into raw material

Tibaut THEYS – PRAYON TECHNOLOGIES

Prayon Technologies

Introduction

- Production of phosphoric acid by wet-process :

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \longrightarrow 3CaSO_4.2H_2O + 2H_3PO_4$$

apatite — sulphuric acid — gypsum — phosphoric acid

- Instead of $Ca_3(PO_4)_2$:

$$(Ca,Na_2,Mg)_{10}\ (PO_4)_{6-x}\ (CO_3)_x\ F_y\ (F,OH)_{2-y}$$

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Introduction

- Phosphate rock contains fluorine, in - more or less - big quantity depending on its origin :
  - Sedimentary rock .... 0,10-0,14 kgF/kgP_20_5
  - Igneous rock .... 0,06-0,08 kgF/kgP_20_5

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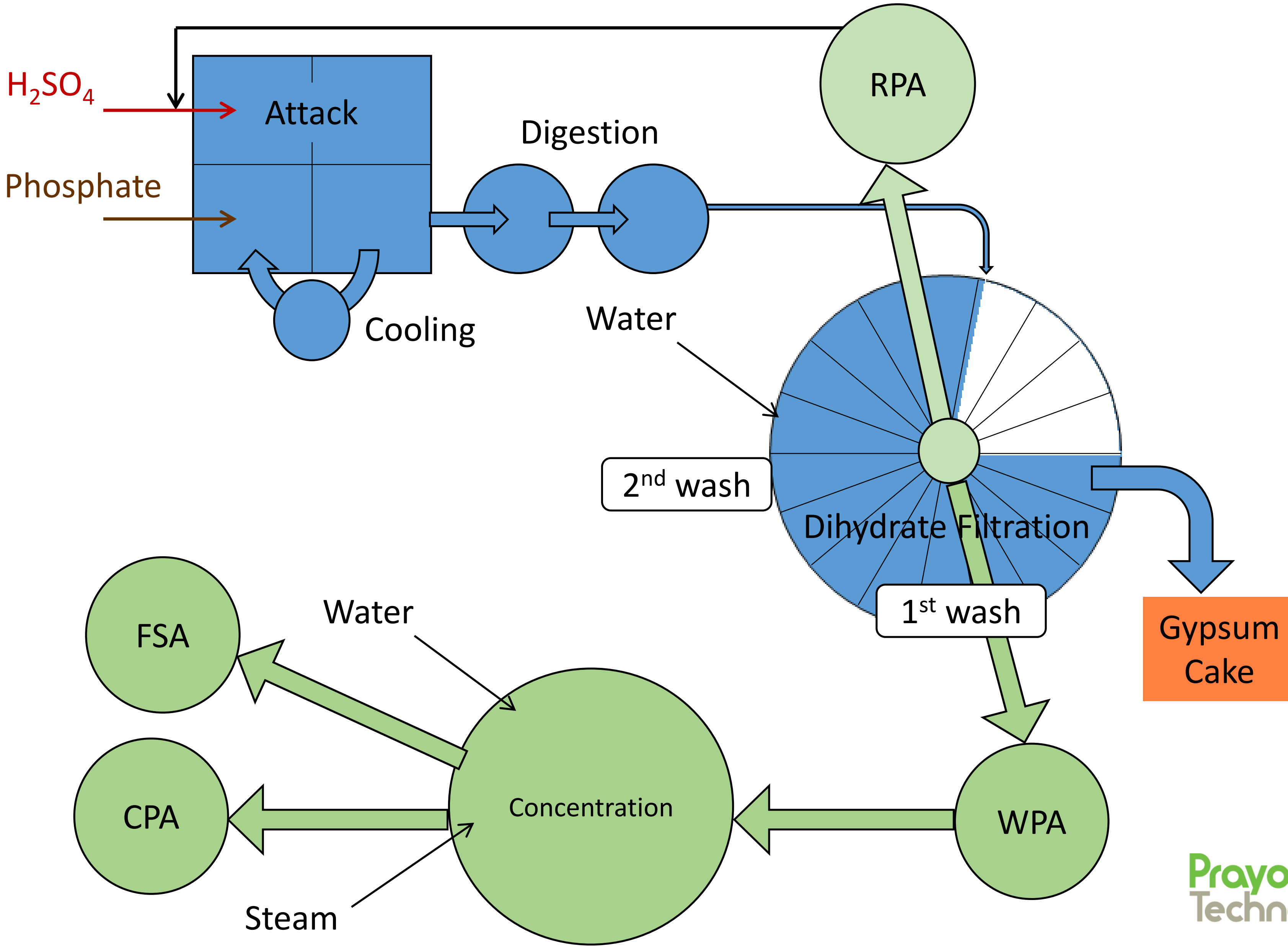
Dihydrate Process - Description



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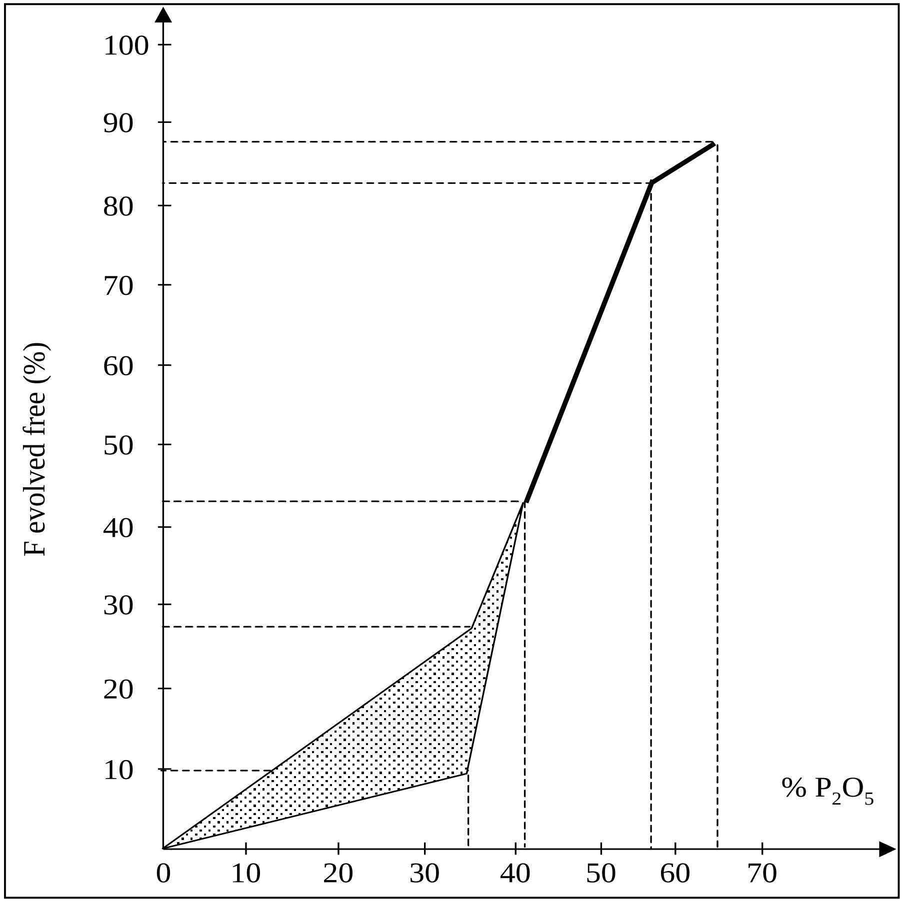
Introduction

- During reaction, fluoride salts will be transformed into volatile fluorinated compounds.
- Fluorine going to the gaseous effluents: 5-10% compared to the initial quantity in the rock.
- Proportion increases with the phosphoric acid strength.
- Gazeous emission have an impact on health and environment.
  - Human tolerance (24 h) : 0,2 mg HF / m³ air
  - Vegetation tolerance (24h) : 0,002 mg HF / m³ air



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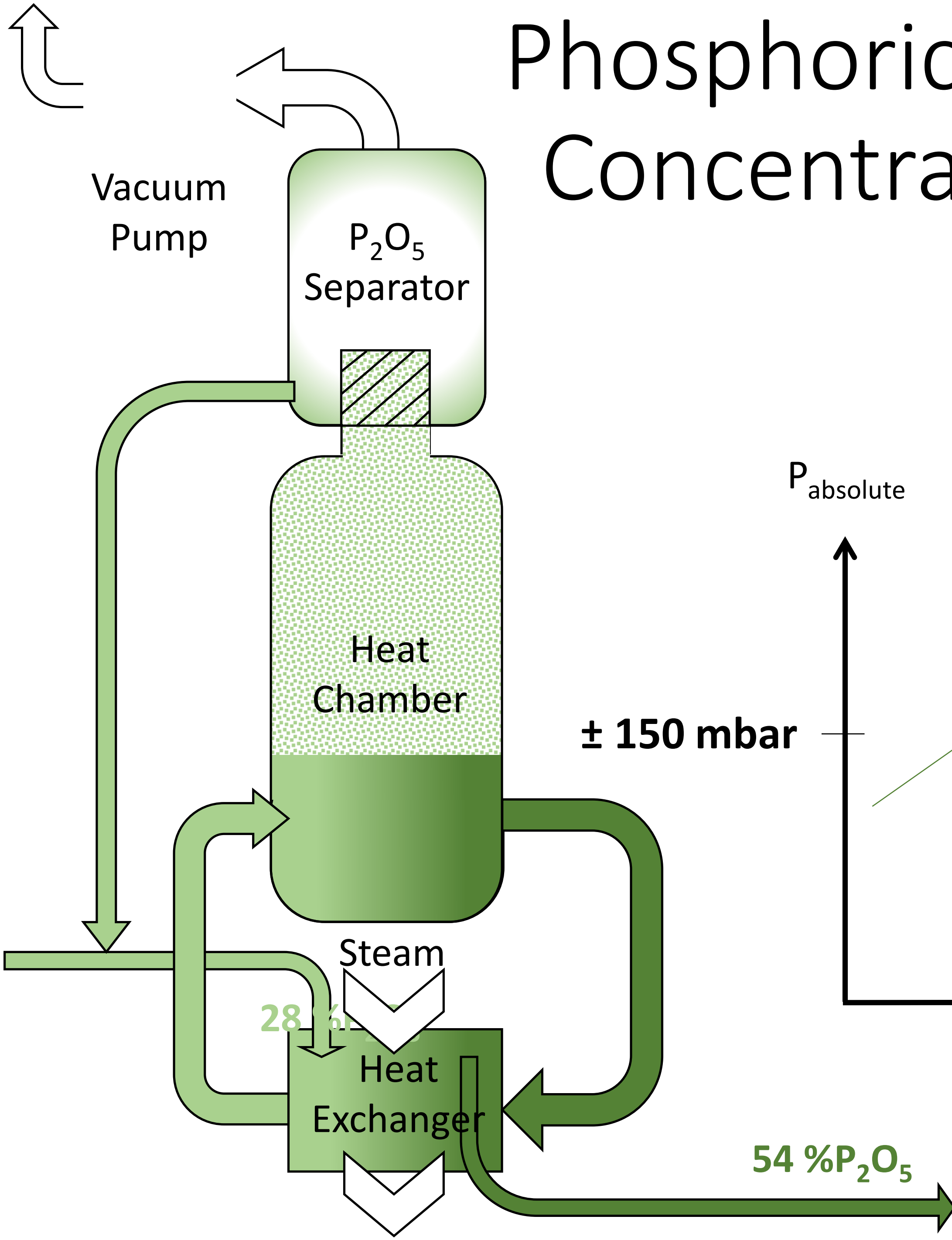
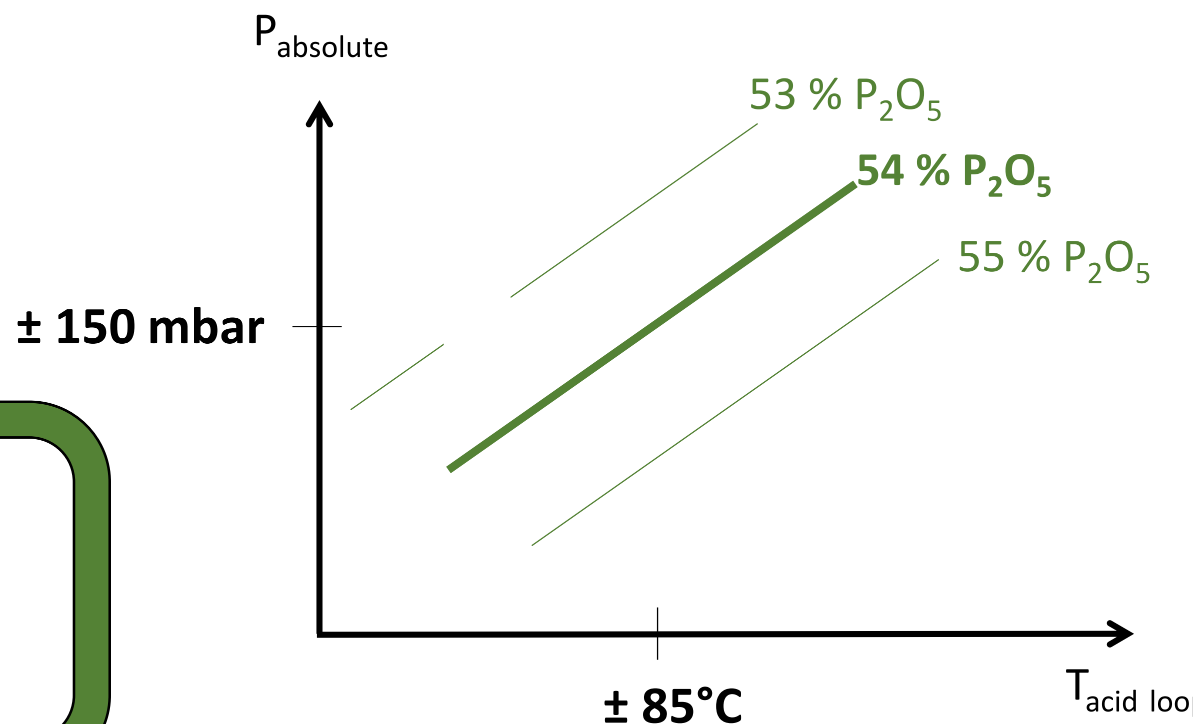
Introduction

- Fluorine need to be collected.
  - Gas scrubber.
  - Flash cooler (HH process)
  - Fluorine recovery system
- Fluorine collected can be neutralised, recycled or processed.
- Due to time limitation, this presentation is limited to the fluorine recovery system of concentration section and an introduction on product applications.

Phosphoric Acid Concentration

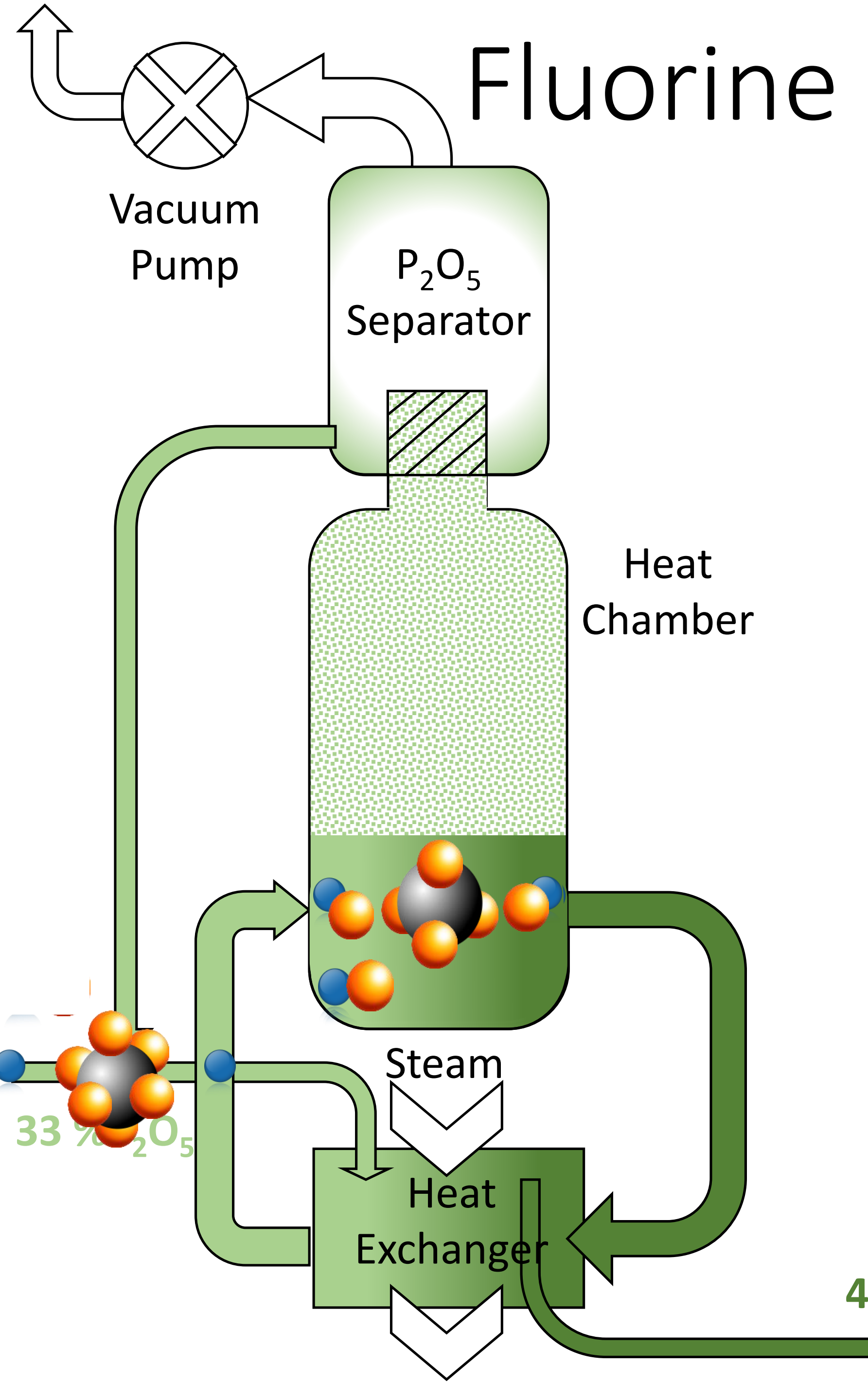


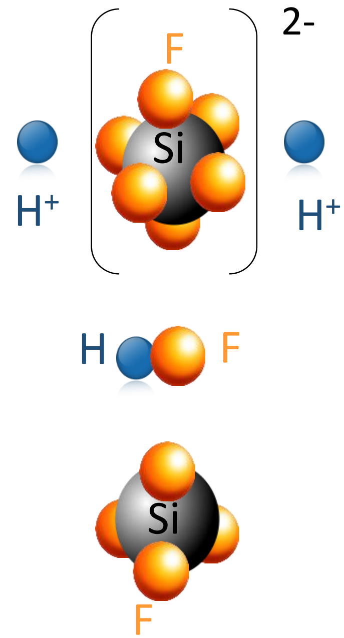


Fluorine absorption

- During concentration F escapes from acid as:
    - HF
    - SiF_4
- The process is based on the washing of vapour with a H_2SiF_6 (fluosilicic acid or FSA) solution sprayed in the gases

Fluorine Evaporation





Hexafluorosilicic acid (H_2SiF_6)

Hydrofluoric acid (HF)

Silicon tetrafluoride (SiF_4)

Boiling point ↓ as absolute pressure ↓

$$H_2SiF_{6\,(l)} \rightleftharpoons SiF_{4\,(g)} + 2\,HF_{\,(g)}$$

$$HF_{\,(l)} \rightleftharpoons HF_{\,(g)}$$

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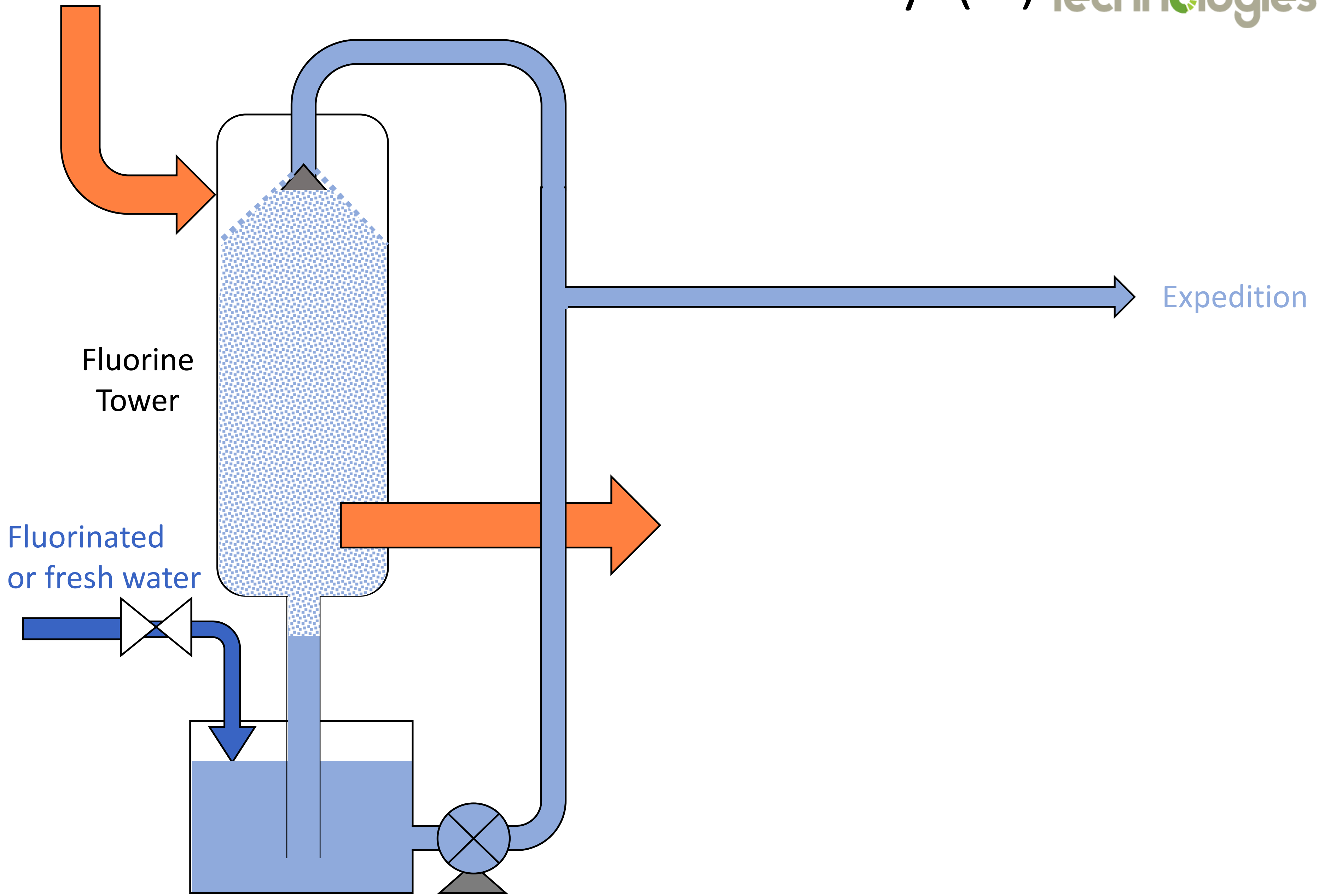
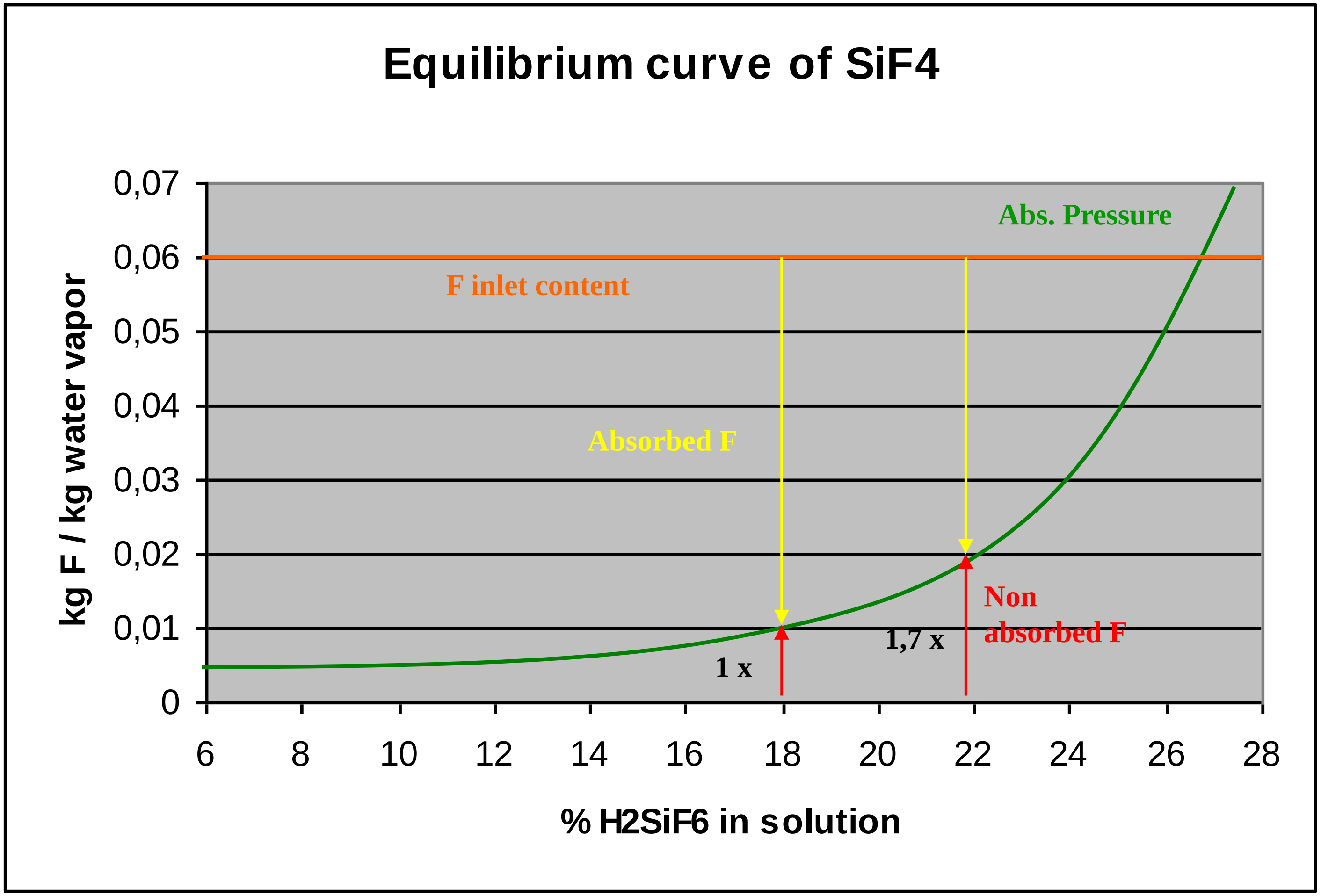
Fluorine Recovery (1)



FSA Recovery



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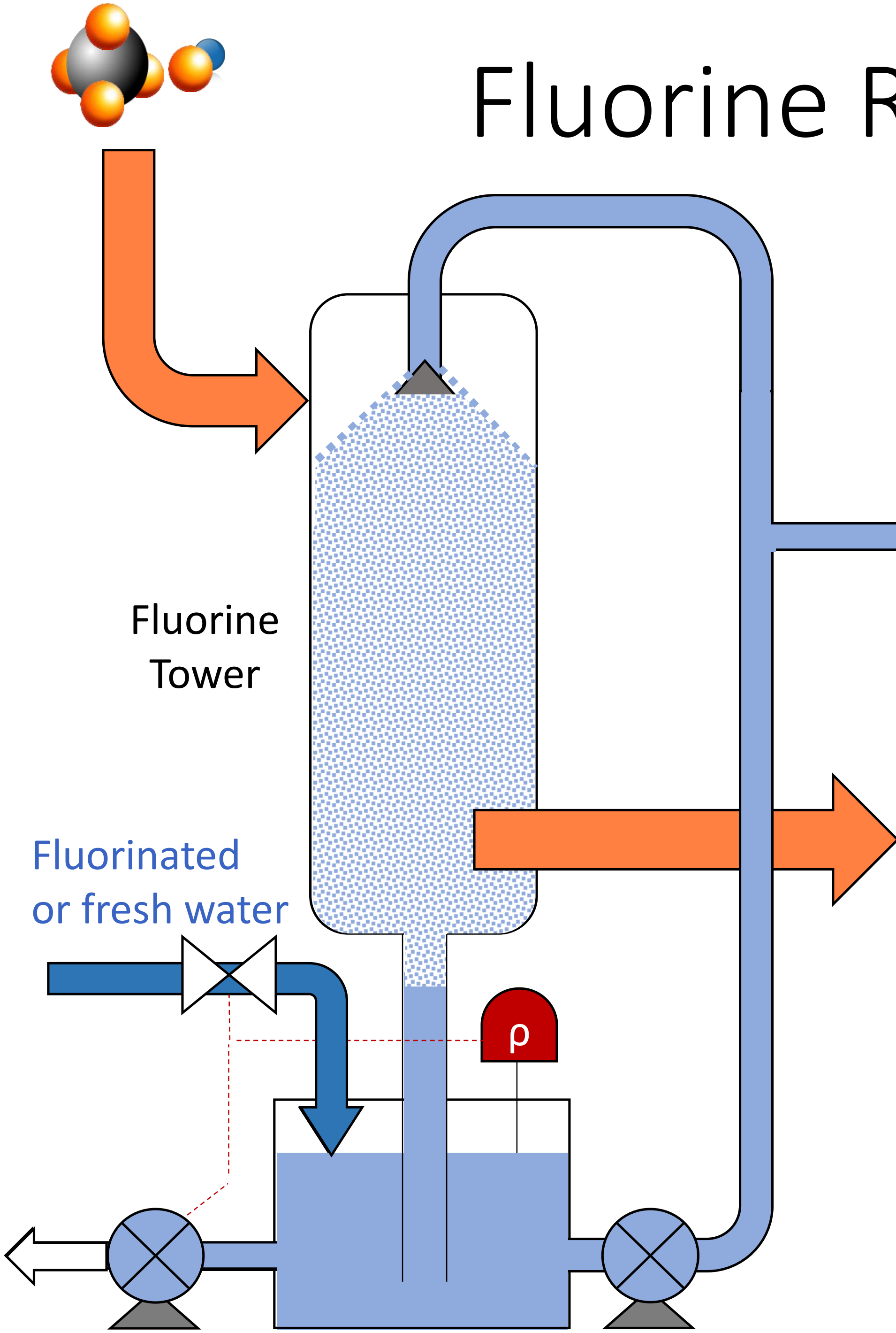
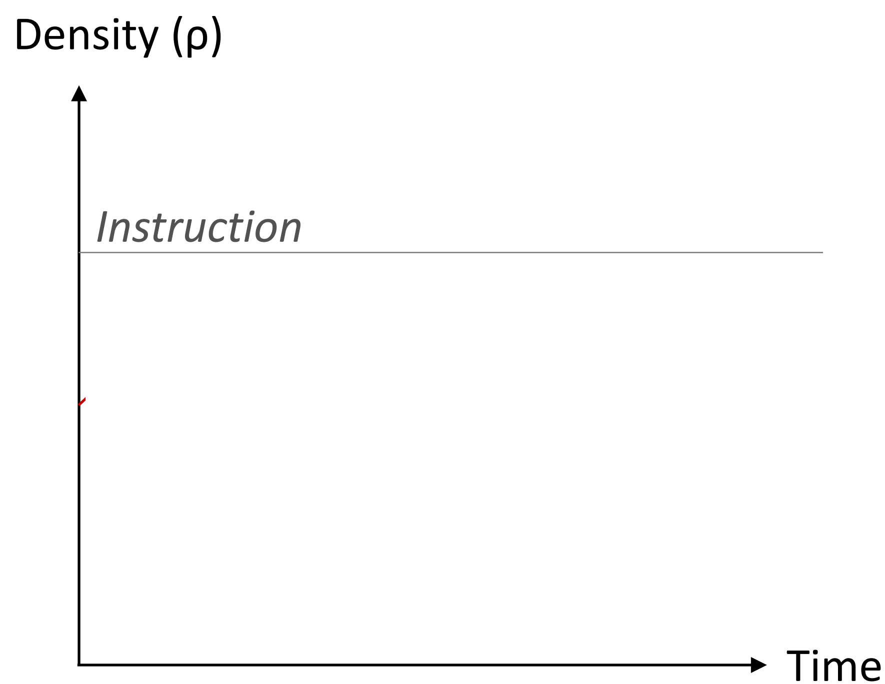
Fluorine Recovery (1)

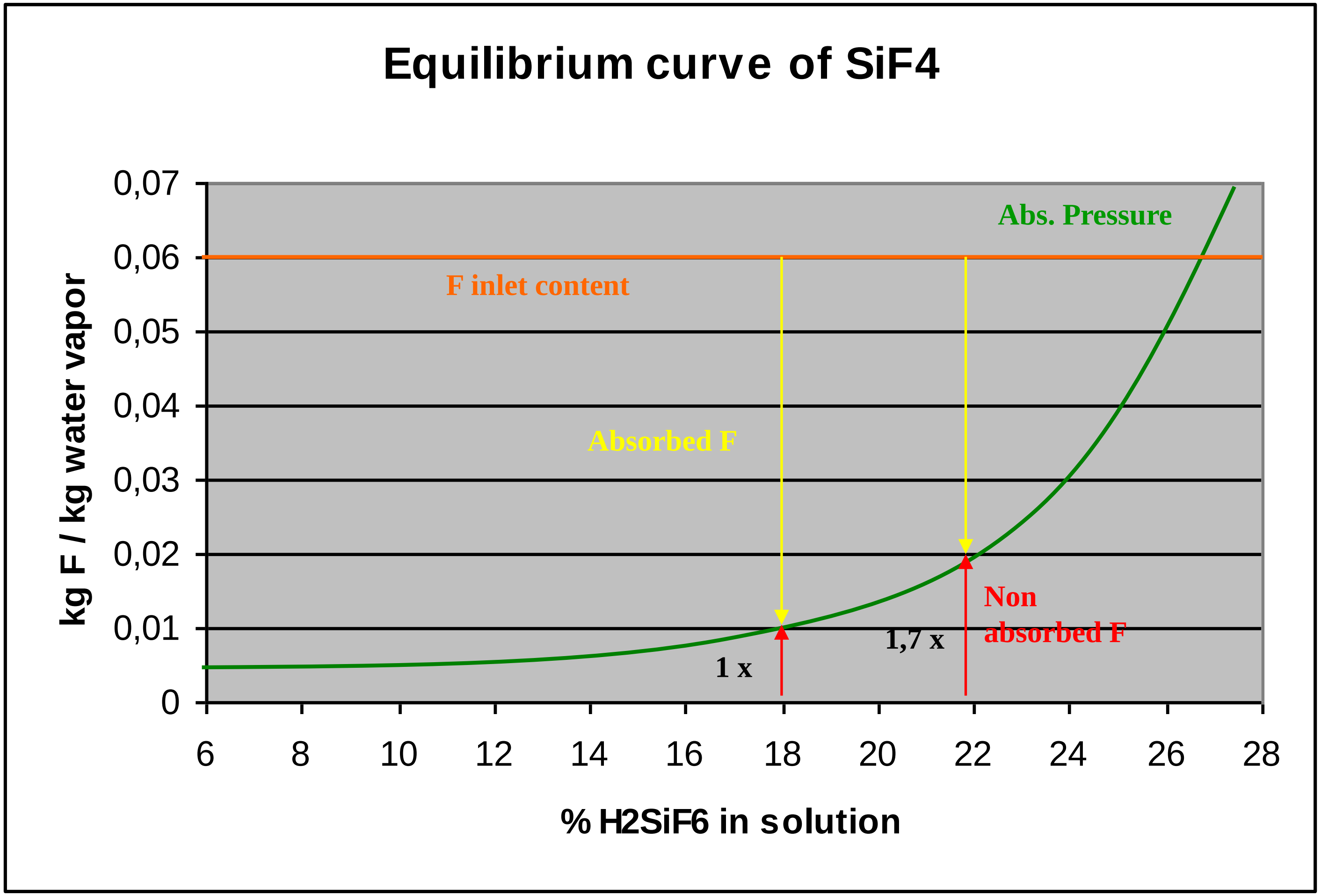


Circulation:

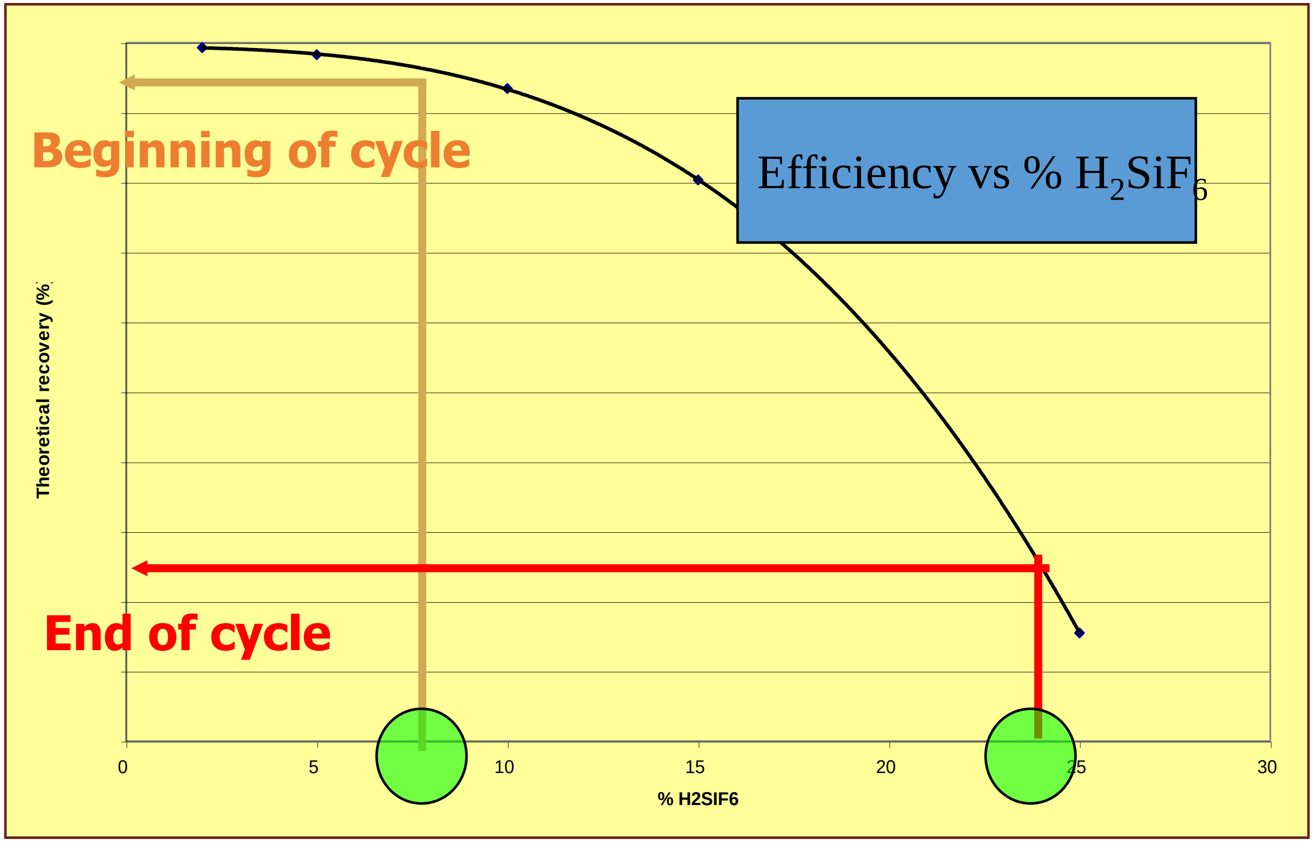
- Continuous cycle
- Batch cycle



FSA Recovery



FSA Recovery



Advantage of batch system

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FSA Recovery

Acid IN	$\%P_2O_5$	**28**	%w/w		
	%F	**2**	%w/w		
Acid OUT	$\%P_2O_5$	**52**	%w/w		
	%F	**1**	%w/w		
Gas	H_2O	**69**	t/t P_2O_5		
	F	**2.18**	t/t P_2O_5		
		Continuous		**Batch**	
%FSA	% w/w	**18**	**22**	**18**	**22**
Recovery	%	**83**	**76**	**88**	**83**
Reference		**1**	**0.91**	**1.06**	**1**

Example : 18% vs 22% FSA

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Fluorine Recovery (2)

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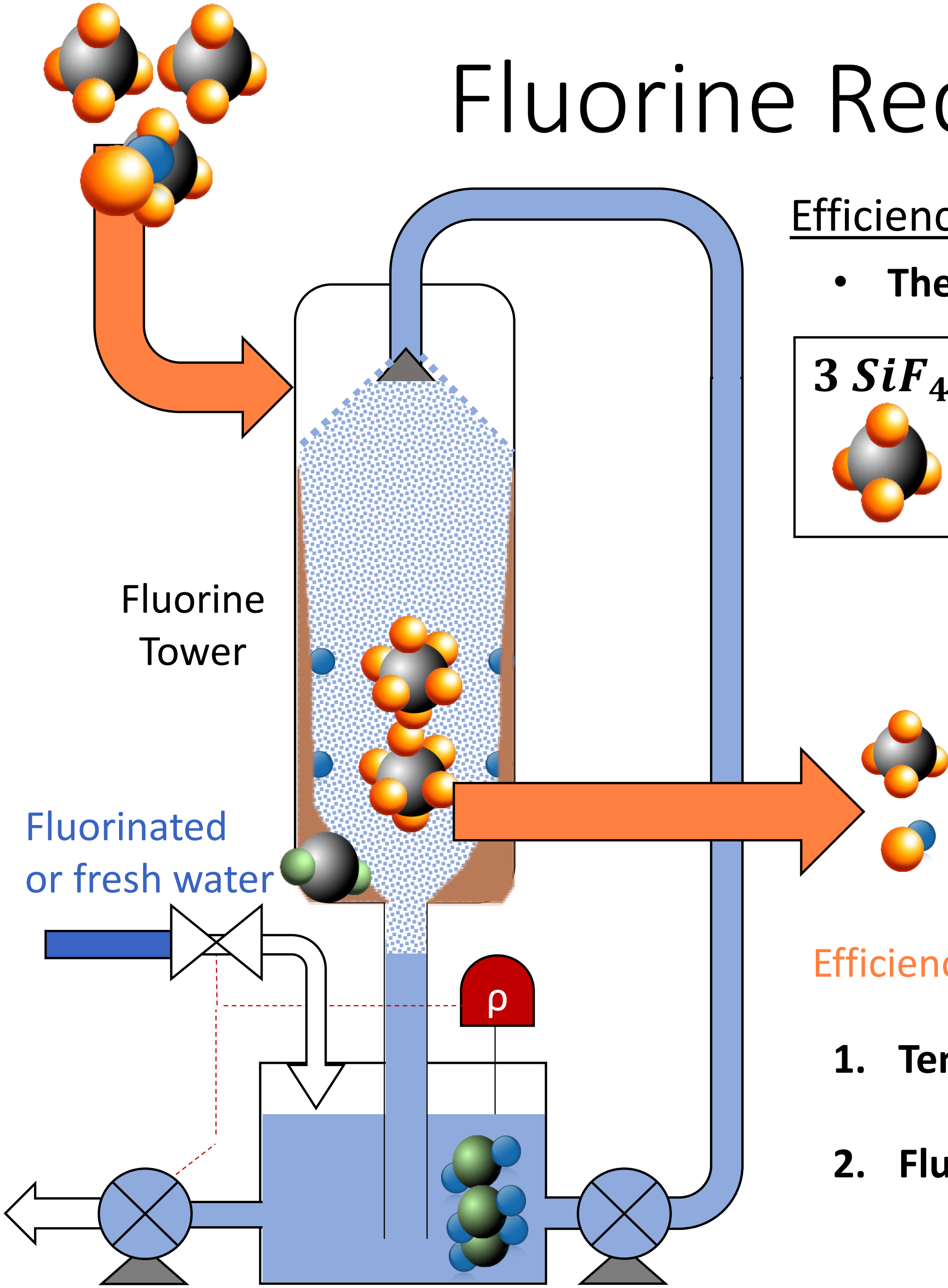


Efficiency of a spraying system:

- **Theoretical efficiency** ↔ Reaction

$$3\ SiF_{4(g)} + 2\ H_2O \rightleftharpoons 2\ H_2SiF_{6(l)} + SiO_{2\ s)}$$

Chemical

$$HF_{(g)} \rightleftharpoons HF_{(l)}$$

Absorbtion

Efficiency depends on:

1. **Temperature** of the spraying solution (**T°**)
   If T°↑ → Efficiency↓
2. **Fluorine content** of the solution **(%H_2SiF_6)**
   If %H_2SiF_6↑ → Efficiency↓

Fluorine Recovery (3)

<u>Efficiency of a spraying system:</u>

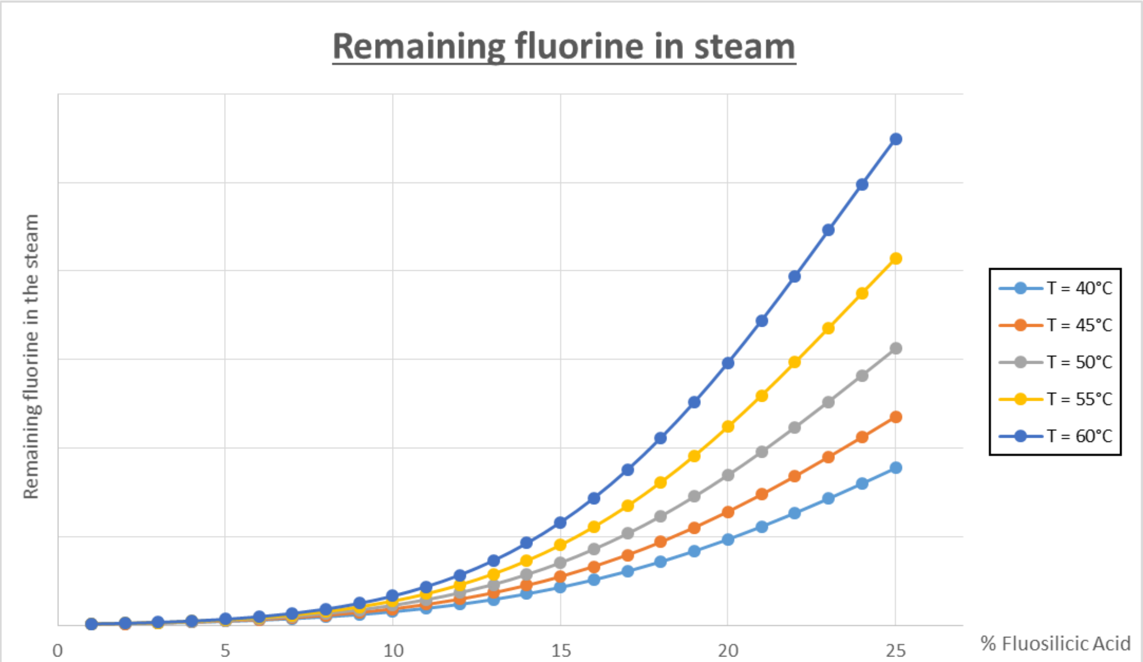
- **Theoretical efficiency** ↔ Reaction

1. **Temperature** of the spraying solution (**T°**)
   If T°↑ → Efficiency↓
2. **Fluorine content** of the solution **(%H_2SiF_6)**
   If %H_2SiF_6↑ → Efficiency↓

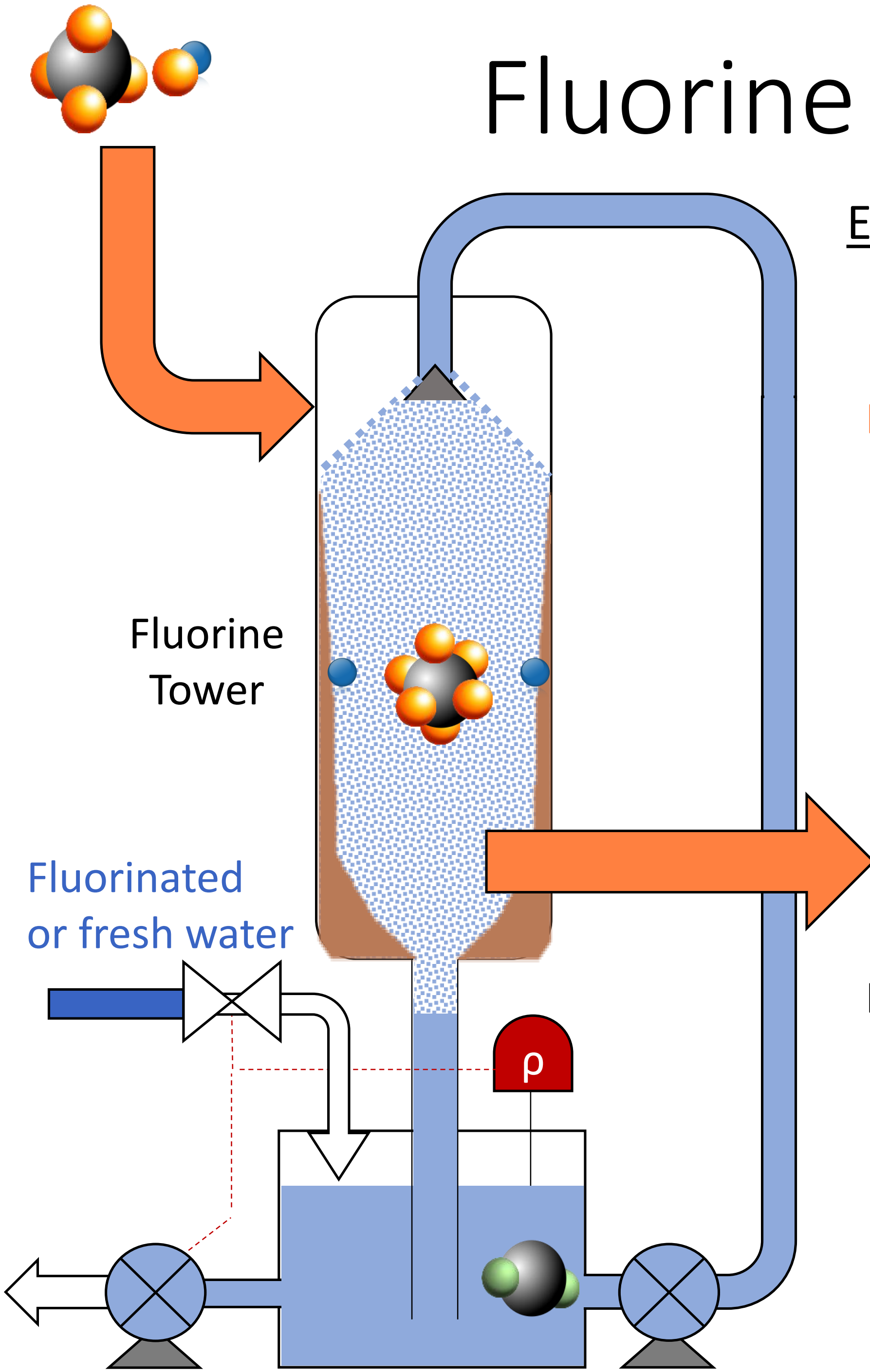
<u>Improvement of **theoretical efficiency**:</u>

Addition of a second spraying tower

%H_2SiF_6↓ (gaseous flow poorer in fluorine)



Fluorine Recovery (4)



<u>Efficiency of a spraying system:</u>

- **Real efficiency** ↔ Mechanical

Mechanical efficiency depends on:

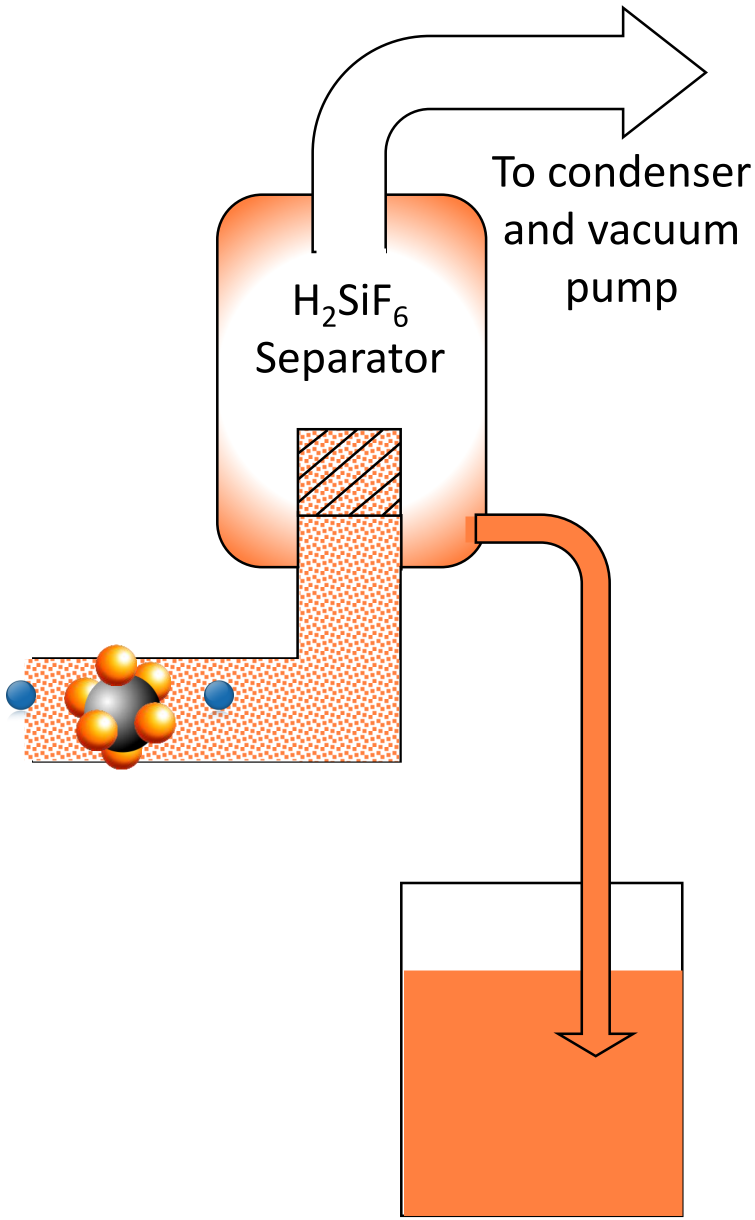
1. Design of the **spraying system** (pressure, flow)
2. Design of the **fluorine tower** (position of the liquid and gaseous outlet, clogging)

H_2SiF_6 Droplets

<u>Improvement of **real efficiency**:</u>

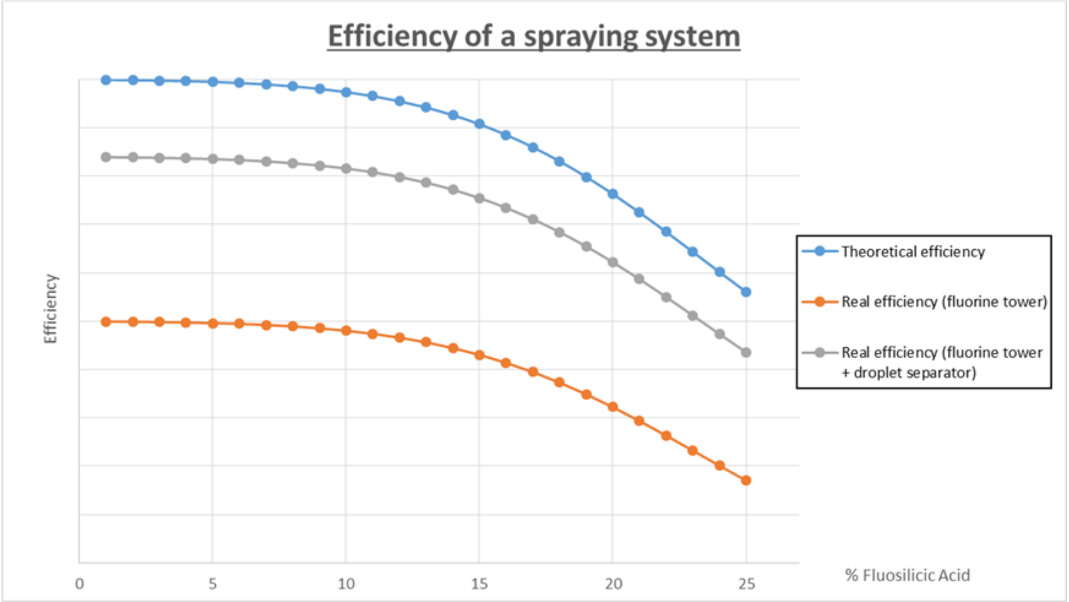
Addition of a droplet separator

Fluorine Recovery (5)

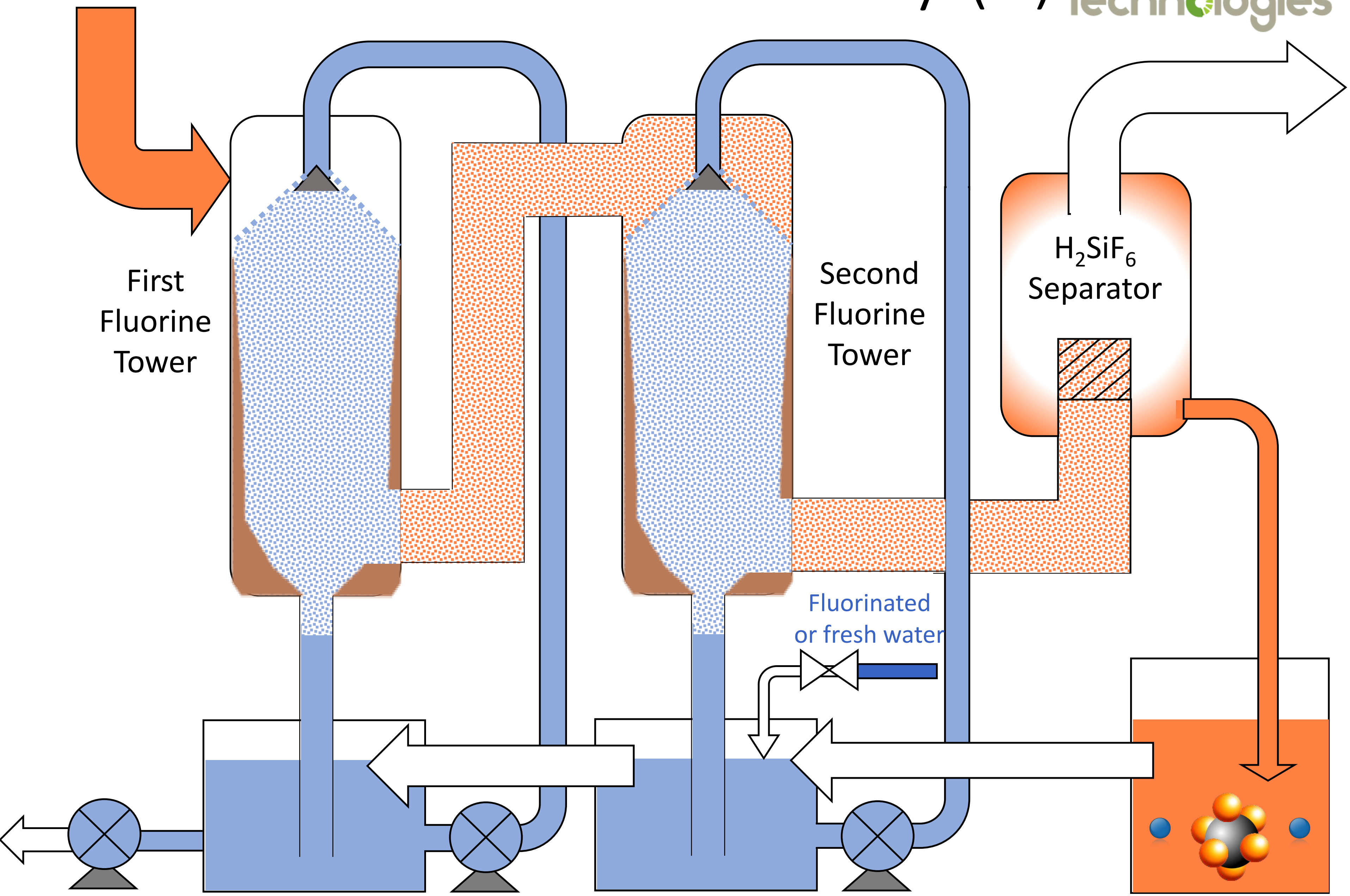


Improvement of **real efficiency**:

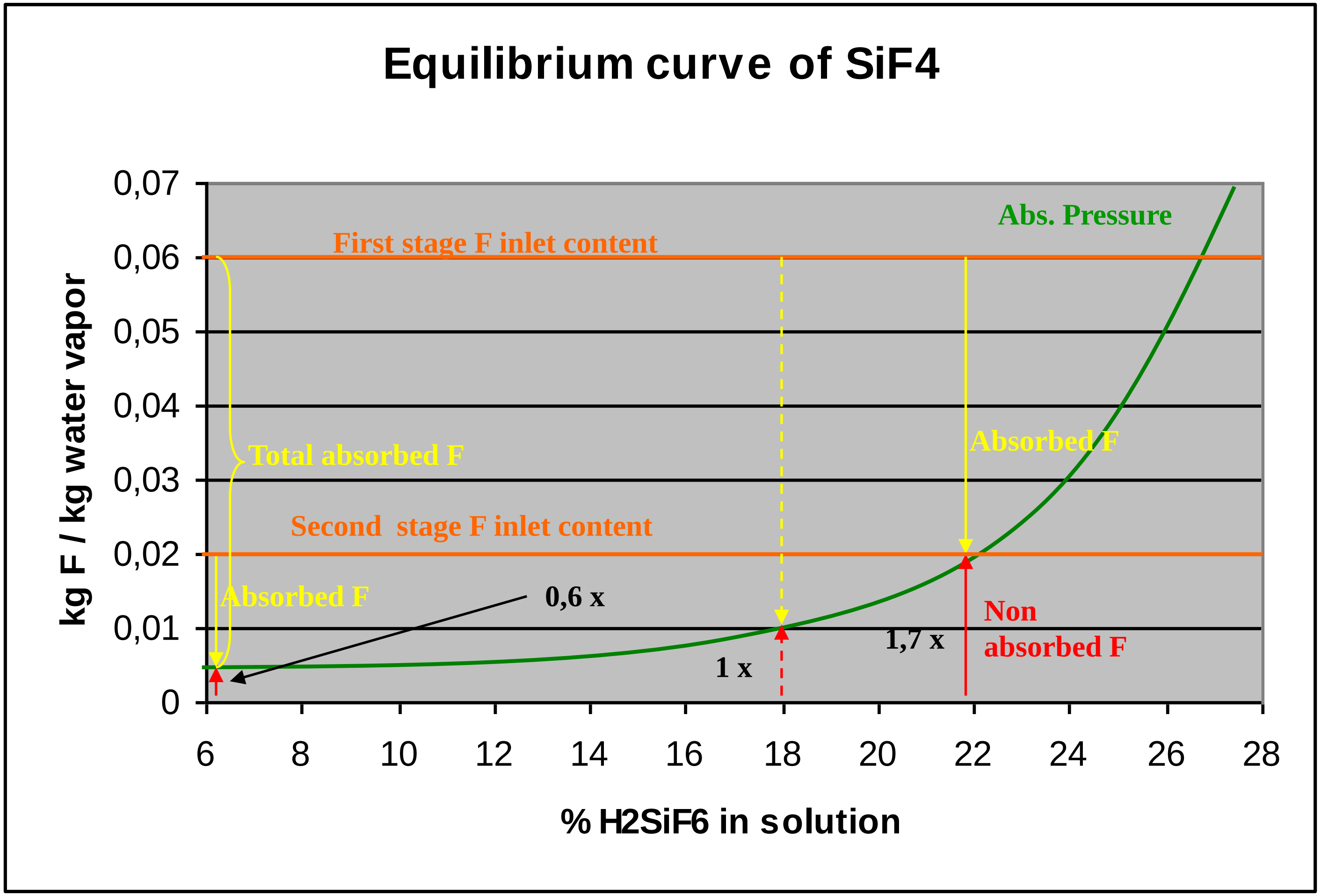
Addition of a droplet separator



Fluorine Recovery (6)



FSA Recovery



FSA Recovery

Acid IN	$\%P_2O_5$	**28**	%w/w	
	%F	**2**	%w/w	
Acid OUT	$\%P_2O_5$	**52**	%w/w	
	%F	**1**	%w/w	
Gas	H_2O	**69**	t/t P_2O_5	
	F	**2.18**	t/t P_2O_5	
		1 stage		**2 stages**
%FSA	% w/w	**22**		**22**
Recovery	%	**83**		**96**
Reference		**1**		**1.16**

Example : 1 stage vs 2 stages

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Absorption technology

- One of the first processes developed was the "Swift" process.
- Patented and licensed to a large number of companies throughout the world.
- Main disadvantage: size of the fluorine scrubber which was about 10% larger in diameter than the evaporator (minimise vertical velocity of the vapours important as the irrigation rates were many many more times the production rate).
- New technologies are much more compact.
- Possibility to install equipment in limited space area.

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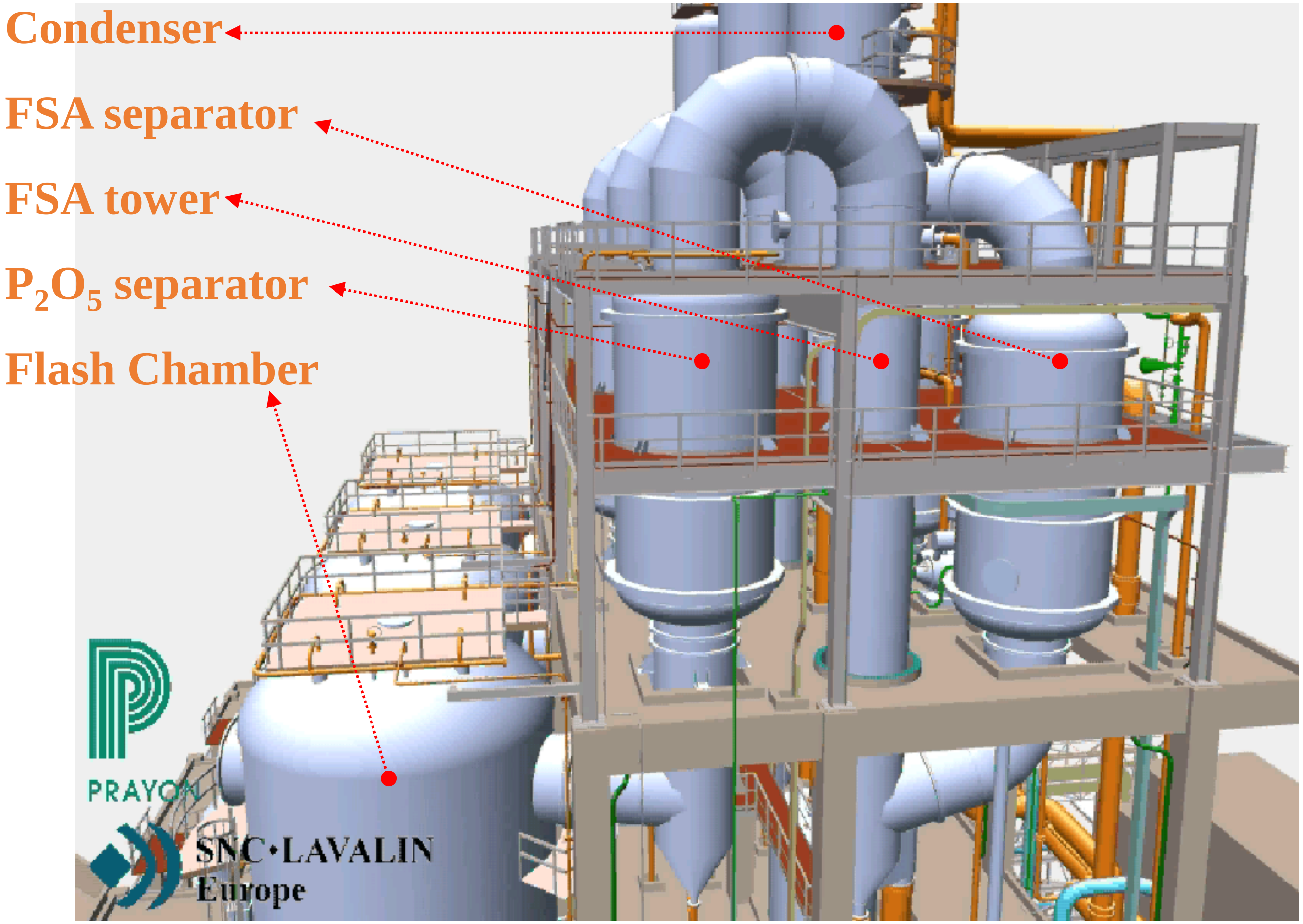
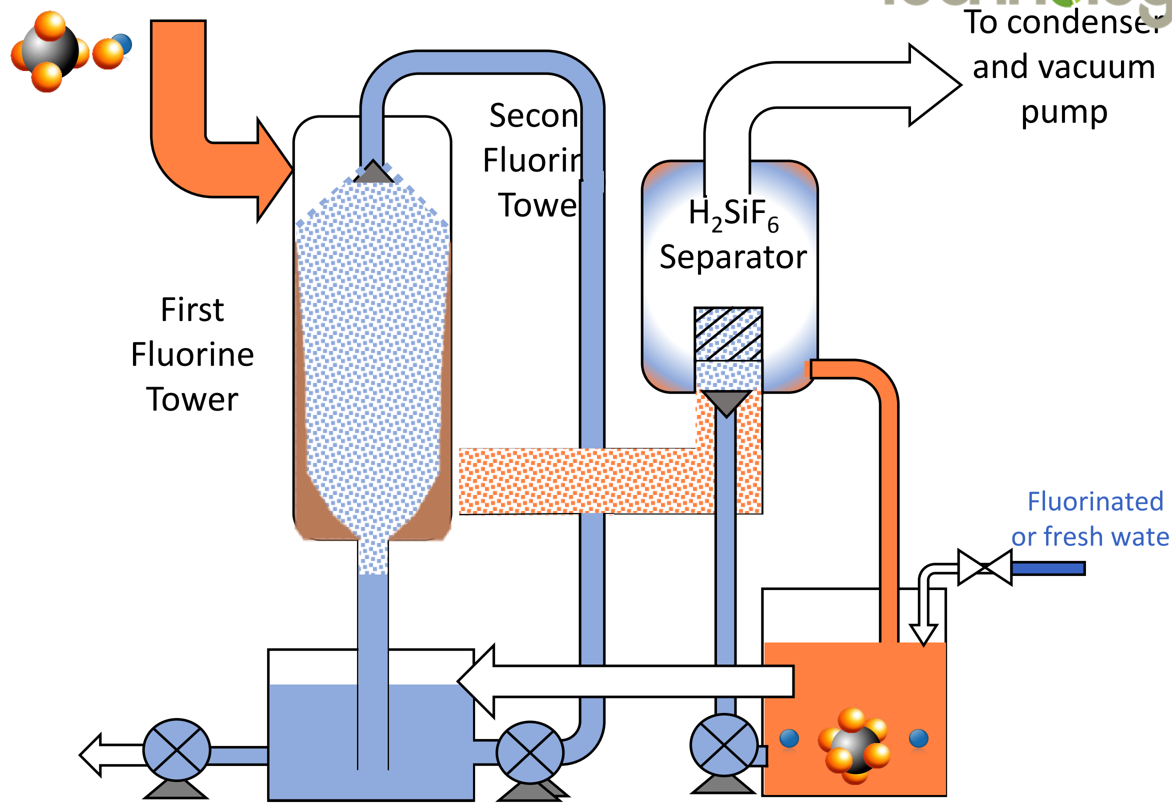
FSA recovery



New Design



<u>Modifications</u>:

- Second Fluorine Tower → **Pipe** between First Fluorine Tower and Separator
- Fluorinated or fresh water **make-up** in the Separator tank
- **Pump** connected to the Separator tank
- No more **tank** on the foot of the ex-Second Fluorine Tower

Features

- **Real efficiency** of the global recovery system remains the same

- Spraying system downstream in the vacuum system produces silica deposit further in the plant → **length of pipe to clean** and **risks of clogging** ↓

- **New design** without the second fluorine tower can be proposed, keeping the global efficiency of the system. High efficiency system installed in limited space area

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FSA Recovery

FSA sprayers

- Proprietary design
- High gap - **<u>low risk of plugging</u>**
- Homogenous spraying - **<u>high efficiency</u>** due to low risk of by-pass

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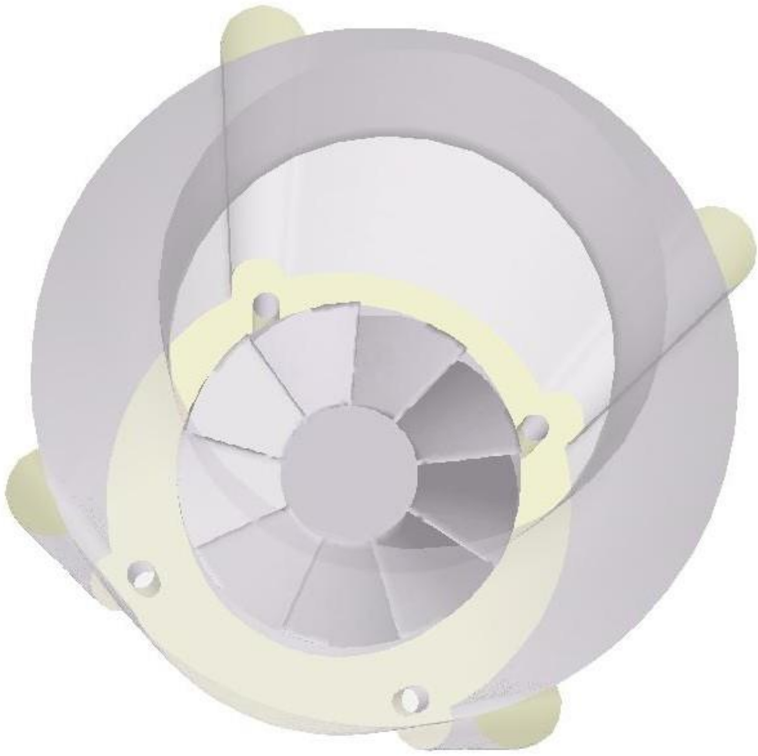
FSA Recovery

CFD simulation



FSA Recovery

PRAYSEP separator

Internal collector

Centrifugal spin

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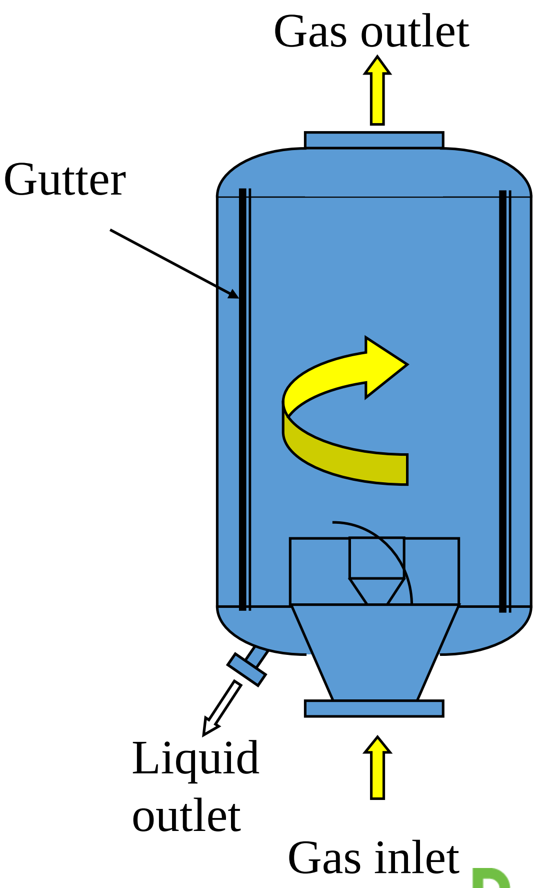
FSA Recovery

PRAYSEP separator

- Reduces the quantity of P_2O_5 in the FSA
- Avoids that the FSA produced goes to the condenser
- 250 ppm in 18% H_2SiF_6 can be achieved with a head loss of around 5 mmHg



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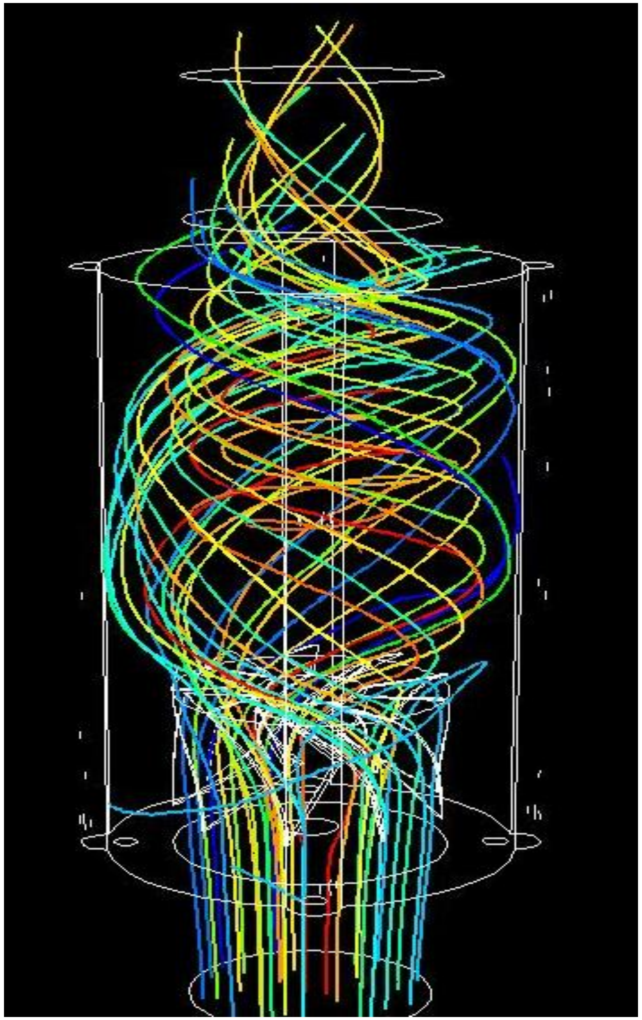
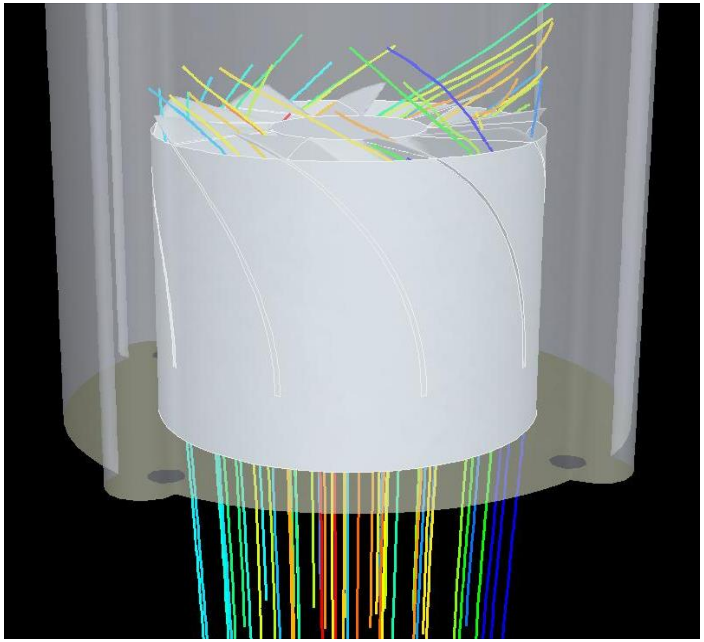
FSA Recovery





Movement of fluid

What to do with this acid?

- Until today FSA is mainly neutralised or dump directly
- Several applications possible
  - Direct use in the fluorination of potable water
  - Production of fluorine salts such as sodium fluoride and aluminium fluoride
  - Production of hexafluorosilicates of sodium (SSF), potassium (PSF) magnesium
  - Production of hydrogen fluoride (HF)
  - Production of SSP and TSP
  - Production of CaF_2

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Addition in potable water

- F added to improve dental health
- CDC (centre for disease control and prevention) recommend 0,7 to 1,2 ppm
- Above 2 ppm risk for health

SSP and TSP production

- Replace part of the H_2SO_4 or H_3PO_4

Sodium and Potassium Salts

- NaF, KF, Na_2SiF_6, K_2SiF_6
- Various usages
  - China industry
  - Steel industry
  - Cement industry
  - Textile industry
  - Toothpaste
- Market very limited

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HF

- Replacement of Fluorspar route
- Main process reactions

  $H_2SiF_6.SiF_4$ (aq) + H_2SO_4 → 2 SiF_4 (g) + 2 HF (aq) + H_2SO_4 (aq)

  5 SiF_4 + $2H_2O$ → 2 $H_2SiF_6.SiF_4$ (aq)+ SiO2 (s)

  2 HF (aq) + H_2SO_4 (aq) → distillation HF (g) + diluted H_2SO_4

  Diluted H_2SO_4 → phosacid plant (DH process)

- Interest of phosphoric acid producers

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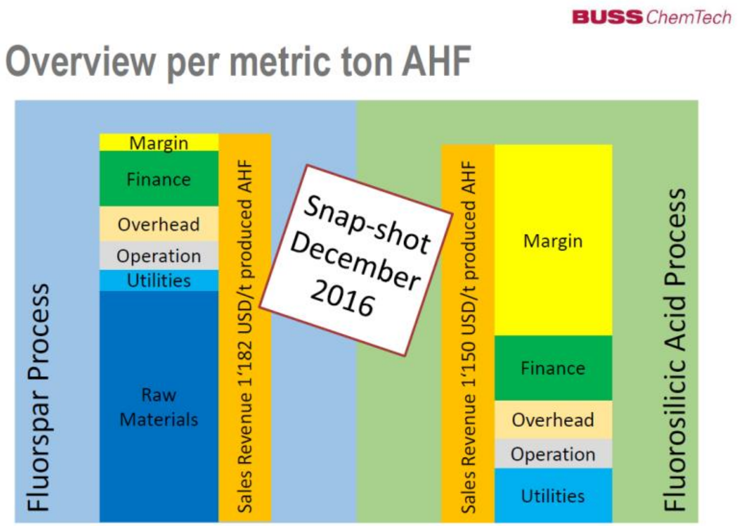
HF

- Seems profitable as raw material is “free”;



- Wengfu is a leader in that field
  - At least 3 plants in operation
    - 2x20 kt and 1x12kt (30kt under commissioning)
- Main technology provider : BUSS technology

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HF

- HF is a very dangerous product
  - Leak
  - Storage
  - Transportation
- Fear of many producers
- Consumer should be close (reductionof transportation risks)

➔ Other paths preferred

AlF3 – low density

- The first process known for manufacturing (LBD) aluminium fluoride from fluosilicic acid was patented by Chemie-Linz, Austria about 50 years ago Chemistry:
- $H_2SiF_6 + Al_2O_3.3H_2O \rightarrow 2\ AlF_3 + 3\ SiO_2 + 4H_2O$
- Low density and low fluidity (flowability) of the product
- This process requires very pure FSA. Quality of the FSA is often a limitation to the use of FSA by this process
- More and more difficult to sell

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AlF3 high density

- Main process reactions

  $H_2SiF_6.SiF_4$ (aq) + H_2SO_4 → 2 SiF_4 (g) + 2 HF (aq) + H_2SO_4 (aq)

  5 SiF_4 + $2H_2O$ → 2 $H_2SiF_6.SiF_4$ (aq)+ SiO2 (s)

  2 HF (aq) + H_2SO_4 (aq) → distillation HF (g) + diluted H_2SO_4

  $Al(OH)_3$ + 3 HF → AlF_3

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CaF2

- HF is mainly produced using Fluorspar (CaF_2) as raw material.
- More than 3 Mt consumed/y
- Quality is decreasing
- Is FSA was converted to CaF_2, world demand could be covered
- NUIF and OCP have issued patents recently

CaF2 – OCP patent

- Base on reaction with ammonia and calcium carbonate

H_2SiF_6 2 H_2O+ 6NH_4OH → 6NH_4F (l)+SiO_2 (s)+6H_2O

NH_4OH can be replaced by NH_3

2NH_4F+$CaCO_3$ → CaF_2 (s)+ CO_2 (g) + 2NH_3 (g) + H_2O

Pilot plant under development

WO2016/171535 A2

THANK YOU !

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