5-3-2018

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

Tibaut Theys
Prayon Technologies, Belgium, ttheys@prayon.com

Follow this and additional works at: http://dc.engconfintl.org/phosphates_viii

Part of the Engineering Commons

Recommended Citation
Tibaut Theys, "Latest Trend for Fluorine in the Phosphoric Industry: Absorption Efficiency Improvement, Conversion into Raw Material" in "Beneficiation of Phosphates VIII", Dr. Patrick Zhang, Florida Industrial and Phosphate Research Institute, USA Professor Jan Miller, University of Utah, USA Professor Laurindo Leal Filho, Vale Institute of Technology (ITV), Brazil Marius Porteus, Foskor-Mining Division, South Africa Professor Neil Snyder, Stellenbosch University, South Africa Mr. Ewan Wingate, WorleyParsons Services Pty Ltd., Australia Prof. Guven Akdogan, Stellenbosch University, South Africa Eds, ECI Symposium Series, (2018).
http://dc.engconfintl.org/phosphates_viii/18

This Abstract and Presentation is brought to you for free and open access by the Proceedings at ECI Digital Archives. It has been accepted for inclusion in Beneficiation of Phosphates VIII by an authorized administrator of ECI Digital Archives. For more information, please contact franco@bepress.com.
Latest trend for fluorine in the phosphoric industry: Absorption efficiency improvement, conversion into raw material

Tibaut THEYS – PRAYON TECHNOLOGIES
Introduction

• Production of phosphoric acid by wet-process:

$$\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{CaSO}_4.2\text{H}_2\text{O} + 2\text{H}_3\text{PO}_4$$

apatite \hspace{1cm} \text{sulphuric acid} \hspace{1cm} \text{gypsum} \hspace{1cm} \text{phosphoric acid}

• Instead of $\text{Ca}_3(\text{PO}_4)_2$:

$$(\text{Ca,Na}_2,\text{Mg})_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_{x}\text{F}_y(\text{F,OH})_{2-y}$$
Introduction

• Phosphate rock contains fluorine, in - more or less - big quantity depending on its origin:
  
  • Sedimentary rock ............... 0,10-0,14 kgF/kgP$_2$O$_5$
  • Igneous rock ............... 0,06-0,08 kgF/kgP$_2$O$_5$
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.
- Gaseous 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
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.
Vacuum Pump

Phosphoric Acid Concentration

$P_{2}O_{5}$ Separator

Heat Chamber

$\pm 150 \text{ mbar}$

Steam

$28 \% P_{2}O_{5}$

Heat Exchanger

$54 \% P_{2}O_{5}$

Vacuum Pump

Prayon Technologies

$53 \% P_{2}O_{5}$

$54 \% P_{2}O_{5}$

$55 \% P_{2}O_{5}$

$\pm 85^\circ C$

$P_{\text{absolute}}$

$T_{\text{acid loop}}$
Fluorine absorption

• During concentration F escapes from acid as:
  • HF
  • SiF₄

• The process is based on the washing of vapour with a H₂SiF₆ (fluosilicic acid or FSA) solution sprayed in the gases
Fluorine Evaporation

Vacuum Pump

$P_2O_5$ Separator

Heat Chamber

Steam

Heat Exchanger

$33 \% P_2O_5$

$45 \% P_2O_5$

Hexafluorosilicic acid ($H_2SiF_6$)

Hydrofluoric acid (HF)

Silicon tetrafluoride ($SiF_4$)

Boiling point ↓ as absolute pressure ↓

$$H_2SiF_6 (l) \rightleftharpoons SiF_4 (g) + 2 HF (g)$$

$$HF (l) \rightleftharpoons HF (g)$$
Fluorine Recovery (1)

Fluorine Tower

Fluorinated or fresh water

Expedition
FSA Recovery

Equilibrium curve of SiF₄

% H₂SiF₆ in solution

kg F / kg water vapor

F inlet content

Absorbed F

Non absorbed F

Abs. Pressure

1 x

1,7 x
Fluorine Recovery (1)

Circulation:
- Continuous cycle
- Batch cycle

Density ($\rho$)

Expedition

Instruction

Time
FSA Recovery

Equilibrium curve of SiF4

Abs. Pressure

F inlet content

Absorbed F

Non absorbed F

1 x

1,7 x

kg F / kg water vapor

% H2SiF6 in solution
FSA Recovery

Advantage of batch system
# FSA Recovery

<table>
<thead>
<tr>
<th></th>
<th>Acid IN</th>
<th>acid OUT</th>
<th>Gas</th>
<th>Continuous</th>
<th>Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>%P₂O₅</td>
<td>28</td>
<td>52</td>
<td>H₂O</td>
<td>69</td>
<td>t/t P₂O₅</td>
</tr>
<tr>
<td>%F</td>
<td>2</td>
<td>1</td>
<td>F</td>
<td>2.18</td>
<td>t/t P₂O₅</td>
</tr>
<tr>
<td>%FSA</td>
<td>18</td>
<td>18</td>
<td>1</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Recovery %</td>
<td>83</td>
<td>76</td>
<td>88</td>
<td>83</td>
<td>83</td>
</tr>
</tbody>
</table>

**Example:** 18% vs 22% FSA
Fluorine Recovery (2)

Efficiency of a spraying system:
• **Theoretical efficiency** ↔ Reaction

\[
3 \text{SiF}_4(g) + 2 \text{H}_2\text{O} \rightleftharpoons 2 \text{H}_2\text{SiF}_6(l) + \text{SiO}_2(s)
\]

Chemical

\[
\text{HF}(g) \rightleftharpoons \text{HF}(l)
\]

Absorption

Efficiency depends on:

1. **Temperature** of the spraying solution (T°)
   
   If T° ↑ → Efficiency ↓

2. **Fluorine content** of the solution (%H₂SiF₆)
   
   If %H₂SiF₆ ↑ → Efficiency ↓
Fluorine Recovery (3)

Efficiency of a spraying system:

- **Theoretical efficiency** ↔ Reaction

1. **Temperature** of the spraying solution ($T^\circ$)
   
   If $T^\circ \uparrow$ → Efficiency $\downarrow$

2. **Fluorine content** of the solution ($\%H_2SiF_6$)
   
   If $\%H_2SiF_6 \uparrow$ → Efficiency $\downarrow$

**Improvement of theoretical efficiency:**

Addition of a second spraying tower

$\%H_2SiF_6 \downarrow$ (gaseous flow poorer in fluorine)
Fluorine Recovery (4)

Efficiency of a spraying system:
• 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)

Improvement of real efficiency:
Addition of a droplet separator

H$_2$SiF$_6$ Droplets
Fluorine Recovery (5)

Improvement of **real efficiency**: Addition of a droplet separator

Efficiency of a spraying system

- Theoretical efficiency
- Real efficiency (fluorine tower)
- Real efficiency (fluorine tower + droplet separator)
First Fluorine Tower

Second Fluorine Tower

H$_2$SiF$_6$ Separator

Fluorinated or fresh water
FSA Recovery

Equilibrium curve of SiF4

% H2SiF6 in solution

kg F / kg water vapor

First stage F inlet content

Total absorbed F

Second stage F inlet content

Absorbed F

Non absorbed F

Abs. Pressure

0,6 x

1 x

1,7 x

Prayon Technologies
## FSA Recovery

<table>
<thead>
<tr>
<th></th>
<th>Acid IN</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%P$_2$O$_5$</td>
<td>28</td>
<td>%w/w</td>
</tr>
<tr>
<td>%F</td>
<td></td>
<td>2</td>
<td>%w/w</td>
</tr>
<tr>
<td>Acid OUT</td>
<td>%P$_2$O$_5$</td>
<td>52</td>
<td>%w/w</td>
</tr>
<tr>
<td>%F</td>
<td></td>
<td>1</td>
<td>%w/w</td>
</tr>
<tr>
<td>Gas</td>
<td>H$_2$O</td>
<td>69</td>
<td>t/t P$_2$O$_5$</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>2.18</td>
<td>t/t P$_2$O$_5$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>1 stage</th>
<th>2 stages</th>
</tr>
</thead>
<tbody>
<tr>
<td>%FSA</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Recovery</td>
<td>83</td>
<td>96</td>
</tr>
<tr>
<td>Reference</td>
<td>1</td>
<td>1.16</td>
</tr>
</tbody>
</table>

**Example: 1 stage vs 2 stages**
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.
FSA recovery

Condenser
FSA separator
FSA tower
P₂O₅ separator
Flash Chamber
New Design

Modifications:

- 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 $\rightarrow$ **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
FSA Recovery

FSA sprayers

• Proprietary design
• High gap - **low risk of plugging**
• Homogenous spraying - **high efficiency** due to low risk of by-pass
FSA Recovery

CFD simulation
FSA Recovery

PRAYSEP separator

Internal collector

Centrifugal spin
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
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$_2$
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 $\text{H}_2\text{SO}_4$ or $\text{H}_3\text{PO}_4$
Sodium and Potassium Salts

- NaF, KF, Na$_2$SiF$_6$, K$_2$SiF$_6$

- Various usages
  - China industry
  - Steel industry
  - Cement industry
  - Textile industry
  - Toothpaste

- Market very limited
HF

• Replacement of Fluorspar route

• Main process reactions
  \[ \text{H}_2\text{SiF}_6\cdot\text{SiF}_4 (\text{aq}) + \text{H}_2\text{SO}_4 \rightarrow 2 \text{SiF}_4 (g) + 2 \text{HF (aq)} + \text{H}_2\text{SO}_4 (\text{aq}) \]
  \[ 5 \text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{SiF}_6\cdot\text{SiF}_4 (\text{aq}) + \text{SiO}_2 (s) \]
  \[ 2 \text{HF (aq)} + \text{H}_2\text{SO}_4 (\text{aq}) \rightarrow \text{distillation} \text{HF (g)} + \text{diluted} \text{H}_2\text{SO}_4 \]

Diluted \text{H}_2\text{SO}_4 \rightarrow \text{phosacid plant (DH process)}

• Interest of phosphoric acid producers
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
HF

• HF is a very dangerous product
  • Leak
  • Storage
  • Transportation

• Fear of many producers

• Consumer should be close (reduction of 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:

  H2SiF6 + Al2O3.3H2O → 2 AlF3 + 3 SiO2 + 4H2O

• 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
AlF₃ high density

• Main process reactions

\[ \text{H}_2\text{SiF}_6\cdot\text{SiF}_4 \text{ (aq)} + \text{H}_2\text{SO}_4 \rightarrow 2\text{ SiF}_4 \text{ (g)} + 2\text{ HF} \text{ (aq)} + \text{H}_2\text{SO}_4 \text{ (aq)} \]

\[ 5\text{ SiF}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{ H}_2\text{SiF}_6\cdot\text{SiF}_4 \text{ (aq)} + \text{SiO}_2 \text{ (s)} \]

\[ 2\text{ HF} \text{ (aq)} + \text{H}_2\text{SO}_4 \text{ (aq)} \rightarrow \text{distillation} \text{ HF} \text{ (g)} + \text{diluted} \text{ H}_2\text{SO}_4 \]

\[ \text{Al(OH)}_3 + 3\text{ HF} \rightarrow \text{AlF}_3 \]
CaF\textsubscript{2}

- HF is mainly produced using Fluorspar (CaF\textsubscript{2}) as raw material.
- More than 3 Mt consumed/y
- Quality is decreasing
- If FSA was converted to CaF\textsubscript{2}, world demand could be covered
- NUIF and OCP have issued patents recently
CaF2 – OCP patent

- Base on reaction with ammonia and calcium carbonate

\[ \text{H}_2\text{SiF}_6 \ 2 \ \text{H}_2\text{O} + 6\text{NH}_4\text{OH} \rightarrow 6\text{NH}_4\text{F} (l) + \text{SiO}_2 (s) + 6\text{H}_2\text{O} \]

NH\textsubscript{4}OH can be replaced by NH\textsubscript{3}

\[ 2\text{NH}_4\text{F} + \text{CaCO}_3 \rightarrow \text{CaF}_2 (s) + \text{CO}_2 (g) + 2\text{NH}_3 (g) + \text{H}_2\text{O} \]

Pilot plant under development

WO2016/171535 A2
THANK YOU !