Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 138 (2016) 240 – 247

Procedia Engineering

www.elsevier.com/locate/procedia

"SYMPHOS 2015", 3rd International Symposium on Innovation and Technology in the Phosphate Industry

# Overview of the fluorochemicals industrial sectors

Alain Dreveton[a,*]

[a]*AD Process Strategies Sarl, Rue Chaponnière 9, CH-1201 Geneva, Switzerland*

**Abstract**

This paper presents a global overview of the industrial sectors producing the fluorochemicals, fluoropolymers with emphasis on applications and requirements for raw materials especially for fluosilicic acid potentially recovered from the conversion of apatite to phosphoric acid.
The various market segments highlighted are water, steel, aluminium, oil refining, nuclear, refrigeration, electronics, solar, glass, pharmaceuticals, agrochemicals, applications for polymers, elastomers, coatings and various other uses.
A tentative estimate of the market segments is provided. The implications on the raw materials, such as volume, expected growth, logistics, etc and consequences for implementing the production process of the end-products are outlined. This overview shall assist to evaluate the size and potential of the various markets and select appropriate outlets for consuming fluosilicic acid as a raw material.


Peer-review under responsibility of the Scientific Committee of SYMPHOS 2015

*Keywords:* fluorochemicals, refrigerants, fluoropolymers, fluoroelastomers,

Fuorochemicals are produced using essentially fluorspar (fluorite mineral) as raw material and more fluorochemicals could be produced from fluosilicic acid recovered by the conversion of phosphate rock to phosphoric acid and phosphate based fertilizers. For the owners of fluorine raw materials, the main question is how to valorize this source of fluorine and how to get the best value out of a downstream production.

This paper is just a partial attempt to answer this question.

* Corresponding author. Tel.:+41 76 578 1249; fax: +41 22 545 7512.
*E-mail address:* a.dreveton@adpro-stg.com


Peer-review under responsibility of the Scientific Committee of SYMPHOS 2015
doi:10.1016/j.proeng.2016.02.081

**Nomenclature**

| | |
|---|---|
| AAGR | Annual average growth rate |
| AlF3 | Aluminium fluoride (AlF3) |
| CVD | Chemical Vapor Deposition |
| FEC | Fluoroethylene carbonate |
| FSA | Fluosilicic acid (H2SiF6) |
| GWP | Global warming potential |
| Halex | Halogen exchange process |
| HFA | Hexafluoroacetone |
| HFE | Hydrofluoroether |
| HFO | Hydrofluoroolefines |
| LIB | Lithium-Ion Battery |
| NA | Non available |
| PTFE | Polytetrafluoroethylene (CF2)n |
| STF | Silicon tetrafluoride (SIF4) |
| TFA | Trifluoroacetic acid |
| TFE | Tetrafluoroethylene (C2F4) |
| UHP | Ultra-high purity |

Global fluorochemicals demand reached 3.16 million tons in 2013 according to Freedonia[1]

At the present time, a very small amount of fluorochemicals is produced from fluosilicic acid (FSA). Only 4 plants worldwide are producing HF from fluosilicic acid and all these plants are located in China and about 10 plants worldwide are producing aluminium fluoride, a low density product (a low quality material). Besides, a single plant in USA is producing silicon tetrafluoride (STF) a precursor for the production of polysilicon. Otherwise FSA is sold as a solution 24% H2SiF6 or converted to sodium fluosilicate for use in fluoridation of potable waters.

The main building block of the fluorine chemistry is hydrogen fluoride (or anhydrous hydrofluoric acid). Other building blocks are elemental fluorine (F2), TFE (tetrafluoroethylene), HFA (hexafluoroacetone), TFA (trifluoroacetic acid), etc. As an example, the fluorine industry supply chain in China is shown below.

Disclaimer: The present paper does not constitute an endorsement of products or forecasts described or and the author or is employer shall not be responsible for the use of this information.

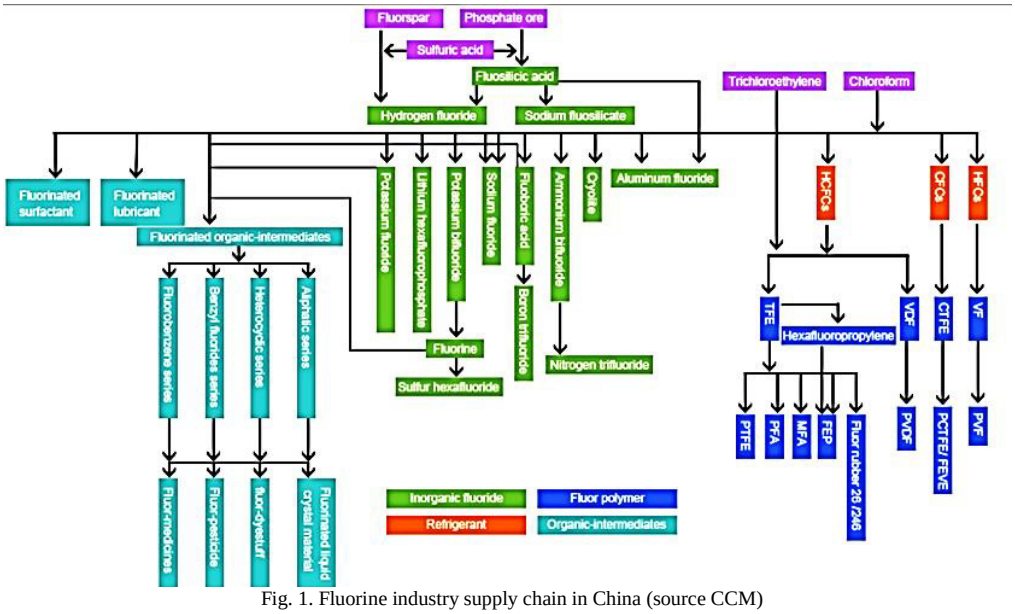


Fig. 1. Fluorine industry supply chain in China (source CCM)

## 1. Inorganic fluorochemicals

The main inorganic substances and downstream products of HF with few applications are listed below:

- AHF — Alkylation (Kerosene), Uranium enrichment (UF6), detergents (LABs linear alkylbenzene sulfonates), F2, other chemicals
- HF diluted — Stainless steel/ alloy pickling, extraction Nb/Ta, Quartz
- UHP HF (Ultra-High Purity) — Semiconductor industry, Solar
- Inorganics — NaF (Technical and USP grade), Na2PO3F, SnF2, CaF2 crystals, KF, LiF, RbF, CsF, Na2SiF6, MgSiF6, NH4F (technical and UHP grade), NH4HF2, BaF2, CaF2 crystals, Na3AlF6, Li3AlF6, KBF4 and salts, NaHF2, KHF2, F2, ClF3 (nuclear), H2TiF6, H2ZrF6, etc
- Fluorine elemental (F2) — IF5, SbF5, WF6, NF3, ClF3, CFx, BrF3, ReF6, CoF3, NF3, WF6, fluorinating agent for fluoropolymers, for cleaning CVD chambers in semi-fab, PV-solar, TFT-LCD panels, SF6, F2/N2, FEC, etc
- Dielectric gas — SF6 (F2 is required for its production), mixture SF6/N2 as substitute
- Electronics gases — NF3, SiF4, WF6, F2 production onsite is about 5’000 mt/y
- Catalysts — BF3, Boron trifluoride diethyl etherate
- Li-Ion Battery electrolytes — LiPF6, LiTFSI (CF3SO2)2NLi and similar, LiBF4, LiAsF6, LiSO3CF3, etc
- Fumigant — SO2F2 banned
- Aluminium — Aluminium fluoride, cryolite for smelting, abrasives, potassium aluminium fluoride for aluminium soldering (Nocolok), K3AlF6, KAlF4, Cs3AlF6, CsAlF4, Rb3AlF6, RbAlF4, RbCsSiF6, K2SiF6, Rb2SiF6, CsRbSiF6, CsKSiF6, NH4CsSiF6
  Many substances are used in flux, in welding electrodes
- Fluorinating agents — SF4, Trimethylamine.trifluoride, etc
- Molten salts

In terms of volume aluminium fluoride and anhydrous hydrofluoric acid which is a main feedstock of fluorochemicals are by far the inorganic fluorochemicals with the largest volumes. The production volume (non-exhaustive list) of most fluorochemicals is provided in Table 2 below.

### *1.1. Aluminium fluoride*

Aluminium fluoride is essentially used as a flux in the production of primary aluminium by smelters. Its specific consumption is about 18 kg/t aluminium metal produced. Based on this consumption and the global aluminium production reported by the International Aluminium Institute of 57 million tons for 2014, the demand of aluminium fluoride of 1’070’000 metric tons can be calculated. Roskill [1] have reported a global consumption of 1’031’000 tons in 2013.

Besides aluminium industry, the demand of aluminium fluoride for ceramics, catalysts, etc is extremely small.

Aluminium fluoride is suffering of a large installed overcapacity in China, almost 100%. In this situation, the projects for aluminium fluoride making sense will be projects with the best economics and a production cost below the 30$^{th}$ percentile on the production cost curve.

### *1.2. Hydrogen fluoride*

The global hydrogen fluoride production excluding its use for the production of aluminium fluoride is calculated based on the total production of acid grade fluorspar (used only to produced HF and AlF3) is 1’320’000 tons in 2014 including about 30’000 tons that are produced from fluosilicic acid.

Roskill [1] have estimated a global consumption of anhydrous hydrofluoric acid of 1’130’000 metric tons for 2013.

Hydrofluoric acid is suffering of the same overcapacity installed as for aluminium fluoride. Furthermore, logistics of AHF is a challenge to be resolved as hydrofluoric is a hazardous material. Many fluorinated substances are regulated which affect its market for fluorochemicals in developing countries.

### *1.3. Inorganic fluorides*

The main applications of fluosilicic acid are shown in below Table 1. The total volume of FSA estimated by HIS [2] was about 260'000 mt in 2013.

Table 1. Uses of fuosilicic acid

| Inorganic fluorides | Estimated global Production mt/y [2013] | Typical application | Trend(*) |
|---|---|---|---|
| Fluosilicic acid | <100'000 | Water fluoridation | +1 |
| Fluosilicates | >100'000 | Water fluoridation | 0 |
| Aluminium fluoride | 90'000 | Aluminium | -1 |
| STF | 30'000 | Polysilicon, Semi/solar | 0 |
| AHF | 30'000 | Chemicals | +2 |
| Subtotal (approx. mt/y) | > 260'000 | | |

Note (*) 0 no growth, +1 slow growth, +2 fast growth

Some minor applications exist as purification of zinc and production of other fluosilicates.
The significant inorganic fluorochemicals (non-exhaustive list) with approximate volume are listed below:

Table 2. Volumes of main inorganic fluorochemicals

| Inorganic fluorides | Estimated global Production mt/y [2013] | Typical application | Trend |
|---|---|---|---|
| AlF3 | 1'031'000 | Aluminium industry | +1 |
| Cryolite | 60'000~~ | Abrasives, aluminium | -2 |
| HF anhydrous | 40'000 (1) | Alkylation (kerosene), LABs (detergents) | -1/+0 |
| HF anhydrous | 34'000 [2012] | Nuclear fuels | +1 |
| HF diluted | 50'000 | Stainless steel, alloy, steel, glass | -1 |
| UHP HF | 100'000~~ | Semi-Fab | **+2** |
| F2 | 28'000 | Fluorochemicals, Semi-Fab | **+2** |
| KF | 30000~~ | Halex fluorinating agent | 0 |
| NaF | NA | Toothpaste, | 0 |
| NH4HF2 | NA | Cleaning, etching, etc | 0 |
| KAlF4 (PAF) | NA | Aluminium brazing | +1 |
| HBF4 | 1'500 | Plating, etc | 0 |
| H2TiF6, other acids | Batch process | Surface treatment | 0 |
| HFSO3 | 30'000 | Catalyst | 0 |
| SF6 | 10'000 | Electric power | -1 |
| ClF3 | 100 | Nuclear | -1 |
| NF3 | 10'000 | Semi-fab, TFT-LCD | -1 |
| SbF3, SbF5 | 50 | Catalyst | 0 |
| WF6 | 500 | Semi-Fab | 0 |
| Na2PO3F | Small | Toothpaste | 0 |
| CFx (Graphite fluoride) | 300 | LIB, lubricant | +1 |
| LiPF6 | 12'000 | LIB | **+2** |
| Subtotal (mt/y approx.) | >> 1'500'000 | | |

Note (*) 0 no growth, +1 slow growth, +2 fast growth

Note (1) Approx. 0.1 pound per barrel for petroleum alkylation

The materials for lithium-ion batteries (LIB) have probably the best growth rate (LiPF6).

Chemicals for semi-conductors, TFT-LCD displays, PV-solar are also growing maybe at lower pace as F2 is a substitute for NF3. F2 has a GWP=0. Many small F2 generators are installed at factories and consuming anhydrous HF. KHF2 material for the bath of the fluorine electrolytic cells is mainly consumed at start- up.

Aluminium is still growing at a sustained pace driven by automotive, aircraft industry, etc.

## 2. Organic fluorochemicals

The main organic fluorochemicals are listed here:

| | |
|---|---|
| • Refrigerants | R134a, R143a, R125, R32, R22, 123 124 R404A, R407A, R407C, R410A, HFO-1234yf, more blends, etc |
| • Foam blowing agent | HFC-345fa (CF3CH2CHF2), HFC-141b, HFC-134a, HFC-152, HFC-227ea, 365mfc,<br>HFO-1233zd(E) trans-1-chloro-3,3,3-trifluoropropene,<br>HFO-1336mzz(Z) (cis-1,1,1,4,4,4-hexafluoro-2-butene will be produced by DuPont in 2016 in China |
| • Spray inhaler propellants | HFC-134a, 227ea |
| • Fluoropolymers | PTFE, PVDF, PFA, etc |
| • Fire extinguishing agents | NOVEC 1230 (C3F7COC2F5), FM200 (HFC-227ea),<br>FE-25 (HFC-125), FE-36 (HFC-236fa 1,1,1,3,3,3-hexafluoropropane),<br>FE-13 (HFC-23) |
| • Semiconductor fabrication | C2F6, CF4, C3F8,<br>C4F8 (hexafluorobutadiene-1,3 (4’000 mt/y) |
| • Pharma/agro intermediates | ETFA (Ethyl fluoroacetate)<br>HFIP Hexafluoroisopropanol (Precursor to Servofluane), |
| • Pharmaceuticals | Anesthetics servofluane, fluorobenzene,<br>Methyl fluoroacetate is the basic material for producing enoxadin, tosufloxacin, 5-fluorouracil,<br>floxuridine, tegafur, 5-fluoro-4-hydroxylpyrimidine and so on<br>Ethyl fluoroacetate is used to synthesize 5- fluorouracil and 5-fluoroancymiol, etc |
| • Coatings | perfluoropolyethers surface modifier (coatings / paints),<br>Mainly co-polymers |
| • Agrochemicals | Herbicide Fluroxypyr, Trifluralin (~40’000 mt/y) |
| • HFA (hexafluoracetone) | CF3COCH3, BTFA, HFIP, HFA.hydrates, Servofluorane |
| • Trifluoroacetic acid (TFA) | ETFA, CF3CONH2, TFAA, TFA, TFE, TFEA, Isofluorane |
| • Triflic acid (CF3SO3H) | Triflic acid, triflates |
| • Dyestuffs | Fluorotriazines, etc |
| • Lubricants | PFPE Perfluoroalkylpolyether (approx. 2’000 mt/y)<br>F−(CF(CF3)−CF2−O)n−CF2CF3 Polyhexafluoropropylene oxide<br>Perfluoromethyether/perfluoroethylether, perfluoropropylether<br>CTFE based lubricants |
| • Heat transfer fluid | HFE-7100, HFE-7200, HFE-7500 |
| • Surfactants | Fluorinated ethylene glycol based, Perfluoro polyether based,<br>Perfluoroalkyl stearate (aqueous acrylic coating surface levelling,..) |
| • Solvents | HFC-365mfc for dry cleaning |
| • Liquid crystals | TFT-LCD screens, |
| • Fluorine elemental (F2) | SF6, UF6, polymers surface fluorination, fluorination of fuel plastic tanks (automotive) |

- Specialties TFE-based, HFE, IF5, etc
- Fluorous phase Perfluorodecalin C10F18, perfluorooctyl bromide C8BrF17
- Blood substitutes Perfluorodecalin
- Fluorination reagents TEA.3HF, etc
- Fluoroaromatics benzotrifluorides, etc
- LIB electrolyte solvent Monofluoroethylene carbonate ~1’500 mt/y
- Energetic materials, etc

The large volume organic fluorochemicals are the refrigerants, the fluoropolymers, fluoroelastomers, specialties, etc

### *2.1. Refrigerants*

As per Chillventa [3], the synthetic refrigerants used in the ventilation, air conditioning and refrigeration technology sector are currently R22, R32, R125, R134a and R143a. R22 is the most widely used around the world, but has actually been banned for new systems in Europe for over ten years. Existing systems may continue to be operated, but a strict refilling ban comes into force for R22 in January 2015.

HFC-134a is now also banned in Europe and replaced by HFO-1234yf.

Table 3. Volumes of main refrigerants

| **Refrigerants** | **Global production mt/y** |
|---|---|
| R22 | 860'000 |
| | Quotas 308’000* |
| R32 | 78’000 |
| R134a | 250’000 |
| R143a | 31’000 |
| R125 | 76’000 |
| HFO-1234yf | NA (1) |
| HFO-1234ze | NA |
| Subtotal (approx. mt/y) | >743’000 |

Note (*): Quotas 2014 for R22 mentioned by Dongyue. Feedstock excluded eg for TFE, PTFE manufacture.

Note (1): Few plants started or under constructions. Demand about 30’000 tons in 2016, 2017.

The global capacity including feedstock is about 1.3 million tons. The refrigerant industry is again under pressure after phase-out of HFCs with high global warming potential and transition to HFOs.

### *2.1. Fluoropolymers*

The fluoropolymers, PTFE (well-known Teflon), PVDF, etc are growing significantly and very fast for PVDF at the moment with many capacity increase and new plants in China.

Table 4. Volumes of fluoropolymers

| Monomers | Fluoropolymers | Global production mt/y | Applications, Industry |
|---|---|---|---|
| TFE | PTFE | 160'000 | Chemical plant, anti-stick |
| VDF (VF2) | PVDF | 65’000 | Chemical plant, membrane, coatings |
| TFE + HFP | FEP | 35’000 | 65% Cable insulation, LAN cable |
| Ethylene + TFE | ETFE | 13’000 | |
| CTFE | PCTFE | | |
| VF | PVF | | Glazing solar collector, laminated steels |
| Ethylene + CTFE | ECTFE | | Flame resistant insulation for wire and cable, aircraft |
| TFE + PPVE Perfluoropropylvinylether | PFA | | |
| TFE + PMVE perfluoromethylvinylether | MFA | | |
| TFE + HFP + VDF | THV | | |
| TFE + PDD Perfluoro-2,2-dimethyl-1,3-dioxole | Tefon AF | | |
| PBVE Perfluoro-3-butenyl-vinyl ether | Cytop | | |
| TFE + Perfluoro Alkyl Vinyl Ether Sufonyl Fluoride | Nafion | | Membranes, chlor-alkali |
| TFE + TTD 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole | Hyflon AD | | |
| Other comonomers PMVE, PEVE, PFBE | | | |
| FE + VE | FEVE | | Coatings for plastics |
| Fluorosilicones | | | |
| Phosphazenes | | | |
| Subtotal (approx. mt/y) | | > 273’000 | |

Note (1): 8-10% AAGR - Note (2): Sales in 2012 US$1 billion

### *2.2. Fluoroelastomers*

Fluoroelastomers are estimated to about 30’000 metric tons. Main applications are gaskets including o-rings, cable, tubes, etc.

Table 5. Main types of fluoroelastomers

| Monomers | Comonomers | Typical |
|---|---|---|
| VDF | HFP | Viton A(*) |
| | CTFE | |
| | HPFP | |
| TFE | PMVE | |
| | PP | |
| VDF+TFE | HFP | Viton B |
| | PMVE | |
| VDF+TFE+CSM | HPFP | |
| Subtotal (approx. mt/y) | | |

Note (*): Also Dai-el, Fluorel, Tecnoflon, SKF, Elaftor (All trade names)

### *2.3. Fluorine specialties*

IHS have estimated the market of fluorine intermediates for pharmaceutical and pesticides US$2.4 billion for 2003. It is a market for maximum 60’000 mt of TFE and HF.

About 30% of the pharmaceuticals are containing fluorine: anesthetics, antibiotics, antidepressants, anti-asthma, anti-cholesterol, anti-arthritis, anti-HIV, antipsychotics, anti-inflammatories. About 10 pharmaceuticals are belonging to the best selling with sales of at least US$1 billion.

About 30% of the pesticides are containing fluorine: herbicides, insecticides, fungicides.

In general, fluoropolymers, fluoroelastomers and all building blocks TFE (tetrafluoroethylene), VDF (vinylidene fluoride), HFE (hydrofluoroether), HFA (hydrofluoroacetone), TFA (trifluoroacetic acid) as well as FEC (fluoroethylene carbonate), agro/pharma intermediates are promising segments.

The know-how of the technology, the size of the investment, the knowledge of the market, etc will be an important barrier for new entrants in these markets. This is already the case of many HF/AlF3 production plants not able to grow with downstream productions and remaining sole producers of HF or AlF3.

## 3. Regulated substances

In many countries and for many applications, the usage of some fluorochemicals is banned or restricted. It is therefore necessary to check carefully the regulations. For example:

- Ban of CFCs
- Ban of PFOA and its precursors
- Ban of Perfluorakyl chains longer than C6
- Ban of HCFCs in Europe
- Ban of HFCs in Europe and transition to HFOs has a major impact
- EPA called for a Ban of fluorinated pesticides in USA
- etc

## References

[1] Roskill, Fluorspar Industry Briefing, Issue 1, March 2015
[2] Ray Will, IHS, Fluorpar Symposium 2014, Miami
[3] Chillventa, Presse release