

HEXAFLUOROSILICIC ACID

(HYDROFLUORSILICIC ACID)

Raw Materials, Manufacture, Toxicity and Public Health Concerns As an Active Ingredient in Fluoridation of Drinking Water

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September 2012

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HEXAFLUOROSILICIC ACID

CAS No: 16961-83-4

MOLECULAR: (H₂SiF₆)

Synonyms: Hydrofluorosilicic Acid, Hydrofluosilicic Acid, Hydrtosilicofluodie Acid, Fluorosilicic Acid, Silicofluoric Acid, Fluosilicic Acid

Raw materials

Calcium fluoride, Hydrofluoric acid, Silicon dioxide, Sulphuric acid, Celite

Preparation Products

Ammonium hexafluorosilicate, Sodium fluoroaluminate, Magnesium fluorosilicate, Potassium tetrafluoroborate, Potassium fluoride, Sodium tetrafluoroborate, MAGNESIUM HEXAFLUOROACETYLACETONATE DIHYDRATE, Chromic acid, Potassium fluorosilicate, Magnesium fluosilicate, Magnesium hexafluorosilicate hexahydrate, Sodium tripolyphosphate, Aluminium fluoride, Sodium fluorosilicate, CUPRIC FLUOROSILICATE, Trisodium hexafluoroaluminate, Ammonium fluoborate, Sodium fluoride, ZINC SILICOFLUORIDE, Lead.¹


FLUORSPAR AND WATER FLUORIDATION CHEMICALS

Fluorspar (CaF₂) is the most important fluorine containing mineral. About 52% of fluorspar consumption worldwide is used as starting material for the production of hydrofluoric acid; another 18% is used for aluminium fluoride, the fluxing agent in the aluminium industry; and 25 % for the steel industry as a flux to improve the fluidity of slag in steelmaking. Fluorspar is the commercial name for the mineral fluorite (calcium fluorite) and it is a major raw material source of fluorine. 25% of the fluorspar consumption of the European Union is produced by EU member states, mainly by Spain. A much larger amount is imported from states like China.²

Fluorspar deposits are primarily a byproduct of precious and base metal ores, such as lead, silver or zinc. Fluorspar deposits vary in mineral composition and are not pure. They contain large quantities of silica. Small quantities of rare earth elements (REE), strontium and other elements may substitute for calcium within the fluorspar crystal structure. Fluorspar is used directly or indirectly to manufacture such products as aluminium, gasoline, insulating foams, refrigerants, steel, and uranium fuel. It is used in the manufacture of fluorocarbon chemicals, including fluoropolymers, chlorofluorocarbons (CFC's) , hydrochlorofluorocarbons (HCFC's), and hydrofluorocarbons (HFC's). CFC's, HCFC's, HFC's and Hydrofluoric acid (HF).

¹ http://www.chemicalbook.com/ChemicalProductProperty_EN_CB3726895.htm

² Annex V to the Report of the Ad-hoc Working Group on defining critical raw materials, European Commission Enterprise and Industry Directorate General.



HF is used as the feedstock in the manufacture of a host of fluorine chemicals used in dielectrics, metallurgy, wood preservatives, herbicides, mouthwashes, dentifrices, plastics and water fluoridation.

One of its most common end-products is fluorosilicic acid or hexafluorosilicic acid also known as hydrofluosilicic acid, which is used in water fluoridation. HF is the primary feedstock for the manufacture of virtually all organic and inorganic fluorine-bearing chemicals and is also a key ingredient in the processing of aluminium and uranium. The remaining use of fluorspar consumption is as a flux in steelmaking, in iron and steel foundries, primary aluminium production, glass manufacture, enamels, welding rod coatings, cement production, and other uses or products such as the manufacture of Hexafluorosilicic acid.

Trace elements such as lead and arsenic are present in finished products. Hexafluorosilicic acid is sold as a concentrated solution that contains a significant concentration of HF(aq) to prevent dissociation and hydrolysis of the H_2SiF_6 .

In North America many municipal authorities source the same product using recovered sulphuric acid from acid scrubbers to react with either fluorspar or phosphate rock.

How is it manufactured?

Before fluorspar can be used to make hydrofluoric acid, the raw ore must be physically concentrated and purified. Fluorspar is crushed, ground up and purified by froth flotation. First the lead and zinc sulphides are separated and the fluorspar treated with sulphuric acid forming hydrofluoric acid gas (HF).

The acid grade fluorspar typically contains at least 97 percent calcium fluoride, as well as silica, mixed metal oxides and a trace amounts of arsenic. The HF gas then begins a purification process involving the gas being cooled, purified by scrubbing and condensed.

The crude product may be diluted and sold as an approximately 70 percent hydrofluoric acid solution, or distilled to remove any remaining water and further reduce impurities, and sold as hexafluorosilicic acid (hydrofluorosilicic acid) typically made up to a concentration of 37 to 42 per cent.

The manufacturing process generates tailing waste consisting of lead and zinc sulfides, spent flotation reagents and corrosive process wastewater.

How does it vary from natural calcium fluoride?

Calcium fluoride occurs naturally in many places in groundwater. In trace amounts this is harmless. Many people, however, are getting high levels of fluoride from many sources beyond the trace amounts of calcium fluoride that are considered "safe".

Calcium fluoride is sparingly soluble under standard conditions in the stomach of the human body, in natural water it is insoluble. Calcium fluoride is excreted mainly through the bowel with up to 80% of that ingested being excreted.

In contrast soft waters that contain little appreciable polyvalent cations (calcium, magnesium, rare earth elements, iron, etc.) do not allow for the removal of fluorosilicates and therefore expose an individual to more HF in the gut because the solution lacks "F buffering capacity".

Sodium fluorosilicate is excreted mainly through the bladder with up to 50% of that ingested in healthy adults being excreted. There is further concern regarding exposure to fluorosilicates in humans that may re-associate in the stomach or bladder in low pH environments. One such concern is they may be associated with increased cancer disease.

According to Roholm's toxicology research on fluorine intoxication pertaining to various inorganic fluorides:

H₂SiF₆ (Fluorosilicic Acid) is 25 times MORE lethally toxic than CaF₂ (Calcium Fluoride)

NaF (Sodium Fluoride) is 20 times MORE lethally toxic than CaF₂ (Calcium Fluoride)

Na₂SiF₆ (Sodium Fluorosilicate) is 20 times MORE lethally toxic than CaF₂ (Calcium Fluoride)

AlF₃ (Aluminium Fluoride) is 8.3 times MORE lethally toxic than CaF₂ (Calcium Fluoride)

According to Urbansky, a senior U.S. EPA chemist and expert on water fluoridation chemicals; such compounds may exist in artificially fluoridated drinking water as well as in low pH acidic environments within the human body (i.e. stomach and bladder) after consumption of fluoridated water.³

³ Urbansky Eward Todd, PhD, Fate of Fluorosilicate Drinking Water Additives, Chemical Reviews, 2002, Vol. 102, No. 8

Comparative Toxicity of Inorganic Fluorides:

Extremely toxic

Hydrogen fluoride	HF
Silicon tetrafluoride	SiF ₄
Hydrofluoric acid	HF
Hydrofluorosilicic acid	H ₂ SiF ₆

Very Toxic

Easily soluble fluorides and fluorosilicates	
Sodium fluoride	NaF
Potassium Fluoride	KF
Ammonium fluoride	NH ₄ F
Sodium fluoride	Na ₂ SiF
Potassium Fluorosilicate	K ₂ SiF ₆
Ammonium fluorosilicate	(NH ₄) ₂ SiF ₆

Moderately Toxic

Cryolite	Na ₃ AlF ₆
Calcium fluoride	CaF ₂

Source: Roholm K [1937]. Fluorine intoxication. A clinical hygiene study with a review of the literature and some experimental investigations. London, England: H.K. Lewis & Co.


WHY TOXICITY IS IMPORTANT

Hexafluorosilicic acid is classified as a health, physicochemical and/or ecotoxicological hazard, according to the National Occupational Health and Safety Commission (NOHSC) Approved Criteria for Classifying Hazardous Substances.

Safety standards for hexafluorosilicic acid and its derivative compounds are very important as little data is available examining the toxicological effects such compounds have on human health or the environment. What information that is available from limited clinical studies clearly demonstrates that 1 ppm of hexafluorosilicic acid ingested orally is the equivalent of 25ppm calcium fluoride.

The EU drinking water standard for naturally occurring calcium fluoride is 1.5ppm however the vast majority of drinking water in continental Europe is below 0.3ppm. The newly revised optimal fluoride level in the USA, recommended by the U.S. Department of Health and Human Services, is 0.7ppm. The Irish limit for artificially fluoridated water is 0.8ppm. The natural background level in surface and groundwater in Ireland is generally below 0.1ppm.

The drinking water standards were established for the much less toxic calcium fluoride which is listed as a moderately toxic compound compared to hexafluorosilicic acid, which is categorized as extremely toxic.



All synthetic fluorides are toxic, and naturally occurring calcium fluoride is benign in comparison (in trace amounts of course, since too much of a good thing is no longer a good thing). Sodium fluoride is the most expensive synthetic fluoride, and is used the least to treat in water supplies. It is no longer used in Ireland. In the late 1990's Ireland sourced its Hexafluorosilicic acid from Holland where it was derived from a byproduct waste from the phosphate fertilizer industry when phosphate rock is processed. It is now sourced from Fluorspar mineral rock.

The chemically synthesised more toxic substance is used in the treatment of drinking water due to cost. Even though sodium fluoride is the least toxic synthetic fluoride, this type has been studied extensively, and associated with many adverse health problems. It is well established that there is incomplete toxicological data available on Hexafluorosilicic Acid products used for water fluoridation.

No data is available from the manufacturer or marketers of Hexafluorosilicic acid on:

- Development toxicity
- Teratogenic effects
- Carcinogenic effects
- Mutagenic effects
- Toxicity to animals
- Chronic long term effects on humans
- Ecotoxicity
- Biodegradation

No comprehensive scientific studies have been undertaken on Hexafluorosilicic acid products used for water fluoridation.

Only incomplete studies and analyses exist to test or measure the various dissociated derivative compounds that may exist in treated water and no detailed toxicological assessments exist to demonstrate their safety for human consumption or environmental toxicity.

What is known however, is that people drinking soft water treated with silicofluoride chemicals will be exposed to much greater toxicological and general health risks than individuals drinking hard water treated to the same artificially high fluoride level.

No studies have ever been undertaken on the bioavailability of fluoride with varying source water chemistry in Ireland and no human health studies undertaken either. What is now known, however, is that the highest prevalence of certain diseases and ill health in Ireland (diseases that may be associated with fluoride toxicity) are predominantly located in areas with soft water that is artificially fluoridated.

It is noteworthy that Chapter 10 of the NRC report (NRC 2006a) reviewed available human and animal studies of carcinogenicity, in addition to genotoxicity studies for fluoride, and the committee unanimously concluded that "Fluoride appears to have the potential to initiate or promote cancers."

The U.S. EPA found that “(f)luoride affects thyroid and parathyroid function in humans and animals, elevating thyroid stimulating hormone levels, altering levels of the thyroid hormones T3 and T4, and increasing levels of parathyroid hormone and calcitonin. These changes can affect the rate of formation of bone tissue and the overall rate of bone growth. These effects of fluoride on thyroid function also may be related to the observed dose-related increase in thyroid tumors in animal studies.”⁴

In 2009 the U.S. Office of Environmental Health Hazard Assessment (OEHHA) proposed Fluoride and fluoride salts for review by the Carcinogen Identification Committee (CIC).

The international respected SENES Oak Ridge Centre for Risk Analysis recommend in particular that silicofluorides (especially H₂SiF₆) commonly used to provide fluoride ion in municipal drinking water, should be included in this analysis.

When added to drinking water Hexafluorosilicic acid dissociates into free fluoride ions, it is now accepted that this reaction is not complete with the possibility of some silicofluoride compounds remaining present in drinking water.⁵


It is further known that the following fluorosilicate species may be present in treated water. However current analytical methodologies are not yet available to accurately measure or quantify the level of residual fluorosilicates or fluorosilicon complexes that may be present.

Table 6. Homoleptic and Heteroleptic Aquo-, Hydroxo-, Oxo-, and Fluorosilicate Species Proposed in, Reported in, or Inferred from the Literature (Gas Phase, Nonaqueous/Aqueous Liquid Phase, and/or Solid Phase)

coordination number of the Si ^{IV} center	fluorosilicates	aquo/hydroxo /oxosilicates	aquo/hydroxo/ oxo/fluorosilicates
6	SiF ₆ ²⁻ HSiF ₆ ⁻	Si(OH) ₄ (H ₂ O) ₂	SiF ₅ (H ₂ O) ⁻ SiF ₅ (OH) ²⁻ SiF ₄ (OH) ₂ ²⁻ SiF ₄ (H ₂ O) ₂ SiF(OH) ₂ (H ₂ O) ₃ ⁺ SiF ₄ (OH) ⁻
5	SiF ₅ ⁻ HSiF ₅	Si(OH) ₅ ⁻	
4	SiF ₄	Si(OH) ₄ SiO(OH) ₃ ⁻ SiO ₂ (OH) ₂ ²⁻	SiF ₃ (OH) SiF ₂ (OH) ₂ SiF(OH) ₃
3	none	SiO(OH) ₂ SiO ₂ (OH) ⁻	Si(OH) ₂ F ⁺

⁴ Evidence of the carcinogenicity of Fluoride and its salts, Reproductive and Cancer Hazard Assessment Branch Office of Environmental Health Hazard Assessment, California Environmental Protection Agency. July 2011,

⁵ Urbansky Eward Todd, Fate of Fluorosilicate Drinking Water Additives, Chemical Reviews, 2002, Vol. 102, No. 8



Once added to water it is established that the liberated fluoride ions will rapidly complex with other cations present in water. This increases their bioavailability in the human body when consumed while free fluoride ions will transform into hydrofluoric acid in the human stomach.

It is accepted by the U.S. EPA that “concentrations of hexafluorosilicic acid may be present in the gastrointestinal tract **after consumption of fluoridated drinking water**”.⁶

The existence of fluorosilicic acid compounds was also noted⁷ by the EU Scientific Committee on Health and Environmental Risks (SCHER), when it published its ‘Opinion on critical review of any new evidence on the hazard profile, health effects, and human exposure to fluoride and the fluoridating agents of drinking water’ – 16 May 2011.

The National Research Council (NRC 2006, pp. 52-53) and Coplan et al. (2007) have discussed the available information on the chemistry and toxicology of these compounds, especially at low pH (e.g., use of fluoridated water in beverages such as tea, soft drinks, or reconstituted fruit juices), when their dissociation to free fluoride ion is probably not complete and individuals are exposed to silicofluorides as a by-product of water fluoridation.

The U.S. EPA have also highlighted that certain toxic fluoride complexes in particular aluminium, iron and other cations may be present in artificially fluoridated water. Dr. Urbansky a senior chemist in the U.S. EPA noted in particular that “*natural waters contain a number of metallic cations that can be ligated by fluoride. **Fluoride binds to trivalent metal cations, such as iron(III) and aluminium, as well as divalent metal cations, such as calcium and magnesium.**” And “much of the fluoride is in fact present as metal complexes, depending on the concentrations of the metal cations, the fluoride anion, and the hydrogen ion.”*⁸

It is also now hypothesized that incomplete dissociated SiF residues may re-associate both at intra-gastric pH and in the bladder which are low pH environments⁹ (thereby exposing the consumer to toxic harm) and during food preparation (low pH soft drinks) producing SiF species including silicon tetrafluoride, (SiF₄), a known toxin. It is also believed that commercial SiFs are likely to be contaminated with fluosiloxanes.

⁶ Urbansky and Schock (2000) Working Document U.S. EPA

⁷ Scientific Committee on Health and Environmental Risks, SCHER, Critical review of any new evidence on the hazard profile, health effects, and human exposure to fluoride and the fluoridating agents of drinking water. May 2011, Page 11

⁸ Edward Todd Urbansky, Fate of Fluorosilicate Drinking Water Additives *United States Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division, Received January 29, 2002, Chem. Rev. 2002, 102, 2837-2854*

⁹ Ciavatta L, et al; “Fluorosilicate Equilibria in Acid Solution”; *Polyhedron Vol 7 (18);1773-79;1988*

POISONOUS SUBSTANCES IN DRINKING WATER

So we now know from scientific study that due to artificial fluoridation of water liberated fluoride ions will form metallic fluoride compounds such as aluminium fluoride.

It is well established that the treatment of drinking water with aluminium sulphate (ALUM) used as a coagulant in water treatment may result in increased aluminium levels in treated water.¹⁰

It is further acknowledged that fluoride ions have a strong tendency to form complexes with heavy metal ions such as aluminium fluoride in water. The toxic potential of inorganic fluorides is mainly associated with this behavior and the formation of insoluble fluorides such as aluminium fluoride (AlF₃).¹¹

In Ireland the *POISONS REGULATIONS, 1982* lists *alkali metal fluorides* as poisons. By adding Hexafluorosilicic acid to water one is not only creating silicofluoride compounds but alkali metal fluorides compounds that are poisonous to public health.

Aluminium fluoride complexes are also created in the stomach at low pH where it acts in competition with hydrofluoric acid. Aluminium fluoride is far more bioavailable than is the free aluminium ion which is quantitatively eliminated out the GI tract. Animal studies have found that aluminium fluoride complexes (AlF₃) in drinking water will result in increased Aluminium levels in the brain and kidney as well as causing significant changes to brain cellular structure and neuronal integrity.¹²


The addition of any substance that is capable of a deleterious or injurious effect upon health is a violation of the Fluoridation of Water Supplies Regulations 2007. Fully or partially dissociated silicofluoride compound may also cause a health hazard because the fluoride ion, the undissociated and the reassociated fluorosilicate and the arsenic and lead present in the chemical are all hazardous to fetal and infant central nervous system development and function.

The Supreme Court Judgment of Ryan v. A.G. (1965) specifically forbids the addition of any amount of substances to water that may be harmful to human health including lead or arsenic. Both arsenic and lead are known to be present in water fluoridation chemicals.

¹⁰ United Nations Environment Programme World Health Organization 1997 International Programme On Chemical Safety Environmental Health Criteria 194: Aluminium

¹¹ International Programme On Chemical Safety Environmental Health Criteria 36 Fluorine And Fluorides, WHO 1984

¹² Varner JA, Jensen KF, Horvath W, Isaacson RL. Chronic administration of aluminium-fluoride or sodium-fluoride to rats in drinking water: alterations in neuronal and cerebrovascular integrity. Brain Res. 1998 Feb 16;784(1-2):284-98.



A recent animal study found significantly higher concentrations of lead in both blood and calcified tissues of animals exposed to both silicofluorides and lead (Sawan et al. 2010). The International Agency for Research on Cancer (IARC) classified inorganic lead as probably carcinogenic to humans (Group 2A) in 2006. The European Food Safety Authority (EFSA) have further identified developmental neurotoxicity in young children and cardiovascular effects and nephrotoxicity in adults as the critical effects of lead exposure.

The U.S EPA has categorised lead as a probable human carcinogen and to have no practical threshold with respect to neurotoxicity (EPA 2004)—in other words, there is considered to be no safe level of lead exposure, and the MCLG for lead is zero (EPA 2009).

It is known that Hexafluorosilicic acid contains lead, regardless of the quantity it is not acceptable to be adding lead to drinking water in any amount.

Furthermore apart from the carcinogenicity of fluoride itself, silicofluoride use is associated with increased blood levels of a human carcinogen, one that is also associated with neurotoxicity and developmental toxicity,¹³

HEXAFLUOROSILICIC ACID BANNED AS A BIOCIDAL PRODUCT IN THE EU.

Hexafluorosilicic acid is used for many industries including the textile, ceramic, steel industry and as a biocidal product.

The same active chemical substance used for water fluoridation was banned as a biocidal substance by the EU in 2006 under Directive 98/8/EC. Hexafluorosilicic acid can no longer be used due to a lack of environmental and toxicological data to demonstrate that it is safe for humans or the environment.

Detailed information was sought by the EU on the toxicology of the substance to include toxicological and metabolic studies, ecotoxicological studies, reproductive toxicity, medical data including medical surveillance data, epidemiological studies on general population, skin sensitivity studies and allergenicity studies, carcinogenicity studies, mutagenicity studies, sub chronic toxicity studies and measures to protect humans and the environment.

No information was provided to the EU. The substance was subsequently removed as an authorized biocide within EU. The phase out date was set as 01/09/2006. The product remains in use in Ireland as the active substance for water fluoridation of drinking water supplies.

¹³ Kathleen M. Thiessen, Ph.D. SENES Oak Ridge, Inc., Center for Risk Analysis Report Submitted to the Cancer Hazard Assessment Branch of the EPA at the request of the International Academy of Oral Medicine and Toxicology (IAOMT) Sept 2011