

# Hexafluorosilicic Acid 2013 Banned Biocidal Product Added to Drinking Water for Fluoridation

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The definition of a biocidal Product is provided in the EU Biocidal Directive (98/8/EC). A biocidal product is any *“Active substances and preparations containing one or more active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means.”* An exhaustive list of 23 product types with an indicative set of descriptions within each type is given Annex V of the directive. Hexafluorosilicic acid is listed in this Directive as a biocidal Product.

The fluoride compounds sodium fluoride and hexafluorosilicic acid, used as water injectable chemicals, are synthesized artificially by industrial reaction and are classed as rodenticides, insecticides and pediculicides, with acute lethal doses in experimental animals comparable to arsenic and lead.<sup>1</sup>

Hydrofluorosilicic acid (and the silicofluorides) are highly dangerous compounds now widely added in public water supplies in countries that support fluoridation of drinking water even though they have never been adequately studied for their toxic effects (as was confirmed by the formal decision on this part by the U.S National Toxicology Program in 2002, nominating fluorosilicic acid for toxicological study because information on this topic was not sufficiently established.<sup>2</sup>

Hexafluorosilicic acid (H<sub>2</sub>SiF<sub>6</sub>) is listed in the EU as a biocide (used for wood preservation and as a herbicidal agent). It has been banned for use as a biocidal product by the European Commission due to lack of toxicological data to demonstrate that it was safe for humans and the environment.<sup>3</sup>

In Australia, Hexafluorosilicic acid is explicitly listed in the Australian classification of toxins as a "DANGEROUS POISON" using the criteria in the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP). The "Material Safety Data Sheet" (MSDS<sup>1</sup>) published in Australia for the compound H<sub>2</sub>SiF<sub>6</sub> specifically lists this chemical as a poison.<sup>4</sup>

In the USA Fluorosilicic compounds were used as pesticides up to 1999. In August 1995, the pesticides act was amended, eliminating fluorosilicate compounds from the registration list and their sale for pesticide use (40CFR153, Subpart H) (U.S. EPA, 1995). In the United States, all pesticide uses have been cancelled (U.S. EPA, 1999). Fluorosilicic acid is listed in Section 8(b) of the USA Toxic Substances Control Act (TSCA; chemical inventory section).<sup>5</sup>

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<sup>1</sup> An MSDS is needed for selling in commerce chemicals that may be dangerous.

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### *What exactly is Hexafluorosilicic acid?*

Hexafluorosilicic acid (*also known as hydrofluosilicic acid or hydrofluorosilicic acid*) is used as an active substance for water fluoridation throughout Ireland and in a few other countries in the World where water fluoridation is practised. The main raw ingredient in the manufacture of this chemical is Fluorspar which is used in the manufacture of Hydrofluoric acid..

Fluorspar is the commercial name for the mineral fluorite (calcium fluorite) and it is the major raw material source of fluorine used in the manufacture directly or indirectly of such products as aluminium, gasoline, insulating foams, refrigerants, steel, and uranium fuel. It is also 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).

HF is the main feedstock chemical used in the manufacture of fluorine chemicals used in dielectrics, metallurgy, wood preservatives, herbicides, mouthwashes, dentifrices, plastics and water fluoridation where fluorosilicic acid or hexafluorosilicic acid also known as hydrofluosilicic acid is the product used in water fluoridation.

Preparation products used in the manufacture of Hexafluorisilicic ( $H_2SiF_6$ ) acid include, 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 and Lead.

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 and other countries many municipal authorities source this product using recovered sulphuric acid containing other dangerous toxic pollutants from industrial acid scrubbers to react with either fluorspar or phosphate rock.

For the later end of the 1990's the chemical used in Ireland was similarly recovered acid from industrial scrubbers imported from the Netherlands. This recovered product is likely to contain variable amounts of other contaminants such as lead, mercury, cadmium, chromium, copper, selenium, barium, boron, arsenic, and thallium<sup>6</sup>. Arsenic is a confirmed type one human carcinogen. Thallium is a radionuclide and emits beta radiation, which makes it by definition a carcinogen.<sup>7</sup>

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It is also considered that commercial SiFs are likely to be contaminated with fluo siloxanes.<sup>8</sup> Fluo siloxanes are classified by Health Canada and Environment Canada as toxic, persistent, and having the potential to bioaccumulate in aquatic organisms.<sup>9, 10</sup>

The European Union has classifies siloxanes compounds as endocrine disruptors<sup>11</sup>, based on evidence that it interferes with human hormone function and a possible reproductive toxicant that may impair human fertility.<sup>12</sup> In laboratory experiments, exposure to siloxane has been shown to cause uterine tumours and harm to the reproductive and immune systems. They are also known to influence neurotransmitters in the nervous system.<sup>13</sup>

### *The Toxicity of Hexafluorosilicic acid*

Accordingly to Roholms data on the toxicological profile of inorganic fluorines<sup>14</sup>, Hexafluorosilicic/Hydrofluorosilicic acid is classified as extremely toxic and is 25 times more lethally toxic than naturally occurring Calcium Fluoride.

Calcium fluoride occurs naturally in many places in groundwater principally in hard waters. In trace amounts this is harmless. Fluoride is not found in naturally in soft waters. In a survey of 650 water samples taken in Ireland prior to commencement of fluoridation in the 1960's fluoride was found in only six water samples.

Fluorosilicates are derivative compounds of hexafluorosilicic acid in water, fluorosilicates are 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

It is well established that there is incomplete toxicological data available on Hexafluorosilicic Acid products used for water fluoridation.<sup>15, 16, 17</sup>

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

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

No comprehensive scientific studies have been undertaken on Hexafluorosilicic acid products used for water fluoridation. Only incomplete studies and analyses exist to

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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.

### *Hexafluorosilicic Acid- A Biocidal Chemical*

The *Biocidal Products Directive* (BPD) also known as the *Biocides Directive* is European Union *Directive*, (98/8/EC), which concerns *biocides*. Hexafluorosilicic acid was listed in the EU as a biocide (used for wood preservation and as a herbicidal agent) until it was banned for use as a biocidal product by the European Commission due to lack of toxicological data to demonstrate that it was safe for humans and the environment.<sup>18</sup>

EU Directive 98/8/EC covers biocidal products placed on the EU market. In the EU biocidal products must not be used, if they are not authorised. Under Annex IIIA of the Biocidal Directive Part iv, Additional data for active substances part VIII; fluoride is a identified substance requiring measures necessary to protect humans, animals and the environment. Fluoride is a list 2 substance under Directive 80/68/EC.

In June 2003 the EU prepared a list of Notified substances, including hexafluorosilicic acid, that were subject to new regulation that required detailed supporting information to be provided to the EU, for the protection of human health and the environment by March 2004.<sup>19</sup>

Hexafluorosilicic acid is listed on page 24 of this document. EC number: 241-034-8; CAS number 16961-83-4<sup>20</sup>

Spain as a manufacturer of this biocide was requested to provide a dossier of information to 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, animals and the environment. A full list of the assessment procedures are provided in pages 33 to 179 of the risk assessment for biocidal products published by the EU.<sup>21</sup>

Where information was not provided the substance could no longer be used as active substance to be sold or marketed as a biocidal product within the EU market.

No information was provided and the substance was subsequently removed as an authorised biocide within EU. The phase out date was set as 01/09/2006.

Despite this the Health Authority in Ireland continues to source Hexafluorosilicic acid

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from Spain for injection into public drinking water supplies to be consumed by the public at large.

Approximately 80% of the population of Ireland are exposed this chemical and its derivative compounds in their drinking water, water which is also used for cooking, bathing, beverage and food production.

Using a "Dangerous Poison" WITHOUT TESTING for human, animal or environmental safety is clearly illegal and an endangerment to public health.

## *CONCERNS HIGHLIGHTED YET IGNORED*

### *U.S National Academy of Sciences, National Research Council*

The U.S National Academy of Sciences, National Research Council highlighted that the toxicological profile of Hexafluorosilicic acid was largely unknown in their report "Fluoride in Drinking Water...A Scientific Review of EPA's Standards" published in 2006.

The NRC report, emphasizes the importance of such testing with questions about incompletely dissociated  $[\text{SiF}_6]^{2-}$  end-products in human diets. It recommends study of silicofluoride treated water (SiFW) of different hardness, mineral content, and silica native to the water, taking into account the reversible equilibrium aspects of  $[\text{SiF}_6]^{2-}$  dissociation. To my knowledge no such studies have yet to undertaken in an attempt to fill the current gaps in scientific knowledge or understanding on the bioavailability of silicofluorides (SiF) in natural drinking water.

In the interest of public safety the NRC listed in excess of fifty comprehensive epidemiological, toxicological, clinical medicine, and environmental exposure assessments requiring detailed investigation.

To my knowledge no such studies have yet to undertaken by Public Health Authorities in any country where fluoridation is still practiced.

### *U.S Environmental Protection Agency*

U.S. senior EPA personnel have found no evidence Silicofluoride (SiF) was ever tested for adverse health effects.<sup>22, 23</sup>(Fox 1999, Thurnau 2000). The health risk from exposure to SiF has been acknowledged by the U.S. EPA who tendered for risk management research to be undertaken on fluorosilicates in drinking water in 2002 and again by the U.S. National Research Council who requested animal testing on the health effects of SiF in 2006. This was confirmed by the formal decision on this part by the US National Toxicology Program in 2002, nominating SiF's for toxicological

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studies on animals because information on this topic was not sufficiently established.

No data is yet available on the results of the toxicological study despite the formal decision to proceed in 2002.<sup>24</sup>

An advisory letter from the Director of the EPA Water Supply and Water Resources Division in a letter<sup>25</sup> dated March 15, 2001 summarizing the position of the highest scientific authorities of the EPA reached in January 2001 noted the following:

*“Several fluoride chemistry related research needs were identified including; (1) accurate and precise values for the stability constants of mixed fluorohydroxo complexes [read “silicofluoride dissociation residues”] with aluminum (III), iron (III) and other metal cations likely to be found under drinking water conditions and (2) a kinetic model for the dissociation and hydrolysis of fluosilicates and stepwise equilibrium constants for the partial hydrolysis products.”*

This communication is an admission by senior EPA management that the Agency are not satisfied with assurances given by their own technical staff of the health safety of silicofluorides on two counts: (i) possible formation of toxic complexes with aluminum, iron and other cations commonly present in water plant water and (ii) potential toxic effects from SiF dissociation residues in municipal drinking water that may be present despite predictions made by EPA and others for SiF dissociation.<sup>26</sup>

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). This request was supported by the international respected SENES Oak Ridge Centre for Risk Analysis recommend in particular that silicofluorides (especially H<sub>2</sub>SiF<sub>6</sub>) commonly used to provide fluoride ion in municipal drinking water, should be included in this analysis.

Despite this formal request which included a submission of detailed supporting evidence, neither fluoride nor silicofluorides were included for carcinogenicity risk assessment. No toxicological tests of any form have been undertaken by the public health authorities in Ireland.

### *European Commission*

Similarly the Director General for Health and Consumers of the European Commission also noted the lack of toxicological information on Hexafluorosilicic acid in the report by the Scientific Committee on Health and Environmental Risks (SCHER) published in 2010 and recommended further examination of the human health risks of fluoridation due to a lack of accurate epidemiological and scientific data.

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In the absence of information proving the safety of this chemical the population continues to be exposed to significant potential dangers. The undertaking of these studies is regarded as of paramount importance for the protection of public health in communities where water fluoridation is practised and one should not wait until proof of toxicity is demonstrated before removing this product from use. Proof of safety must be demonstrated first, yet this serious breach of procedures has been allowed to continue unhindered in Ireland by the EU.

It is deeply disturbing that despite the conclusive findings of scientific bodies both in the USA and EU which highlighted the lack of toxicological data for Hexafluorisilicic Acid, and despite requests for such studies to be urgently undertaken no such studies have been completed or made public, that the chemical continues to be injected into public water supplies for consumption by the entire population regardless of their individual health needs or age.

In light of these facts it is astonishing to observe, in the absence of any toxicological or health risk data, that the Health Authority in Ireland (as well as other fluoridated countries) continue to advise that the chemical is safe for consumers or the environment without any proof to support such a claim.

Science is based on measurable facts not opinion and given the alarming health statistics for Ireland with much greater incidence of certain diseases and health conditions (many that are associated with fluoride toxicity in humans) the public are continually exposed to unnecessary risk.

In such circumstances the HSE and Irish State remain at significant risk of future legal action in supporting the continued intoxication of Irish citizens with an untested hazardous chemical being added to their water supplies.

### *Exposure to Hexafluorosilicic acid and silicofluoride ions*

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.<sup>27</sup>

It is further now known that the numerous fluorosilicate species may be present in treated water after injection with Hexafluorosilicic acid. Alarmingly it is also acknowledged that current analytical methodologies are not yet available to accurately measure or quantify the level of residual fluorosilicates or fluorosilicon complexes that may be present in fluoridated water.

The U.S. EPA have separately concluded that “*concentrations of hexafluorosilicic acid may be present in the gastrointestinal tract after consumption of fluoridated drinking water*”.<sup>28</sup>



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The existence of fluorosilicic acid compounds was also noted<sup>29</sup> 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)<sup>30</sup> 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.

It is now hypothesized that incomplete dissociated SiF residues may re-associate both at intra-gastric pH and in the bladder which are low pH environments<sup>31</sup> (thereby exposing the consumer to toxic harm) and during food preparation (low pH soft drinks) producing SiF species including silicon tetrafluoride, (SiF<sub>4</sub>), a known toxin.<sup>32 33 34 35 36 37 38</sup>

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