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No. 82225-5

SUPREME COURT OF THE STATE OF WASHINGTON

CITY OF PORT ANGELES,

Respondent,

MOTION TO FILE CURIAE BRIEF OF
FLUORIDE CLASS ACTION

v.

OUR WATER-OUR CHOICE and
PROTECT OUR WATERS

Petitioners,

v.

WASHINGTON DENTAL SERVICE
FOUNDATION, LLC,

Respondent.

A. IDENTITY AND INTEREST OF AMICUS CURIAE

Fluoride Class Action is an association that opposes using public water systems
to medicate people. The work of Fluoride Class Action may be viewed by going to the

MOTION TO FILE AMICUS CURIAE
BRIEF OF FLUORIDE CLASS ACTION - 1

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1
2 following web site: <http://fluoride-class-action.com>. It is the aim of Fluoride Class
3 Action inspire class action and consumer protection attorneys to sue municipalities
4 which deliver fluoridated water for harm done to those who consume the water. The
5 aim is to serve as a repository of information about how to proceed with these cases
6 and to make this information available to fellow attorneys.

7 A healthy person stores half of all fluoride ingested mostly in his/her bones,
8 while the person with kidney disease retains 80%, and it is a downward spiral for
9 him/her. See Appendix B-71, Health Effects: Fluoride & the Kidneys,
10 www.FluorideAlert.org. To make a successful case against municipalities it is not
11 necessary to prove that fluoride is the only cause of harms; it is only necessary to prove
12 that fluoride exacerbates health problems and hastens death. For example, the lifespan
13 of any person who died of kidney disease at an early age was probably shortened by
14 consumption of fluoride.

15 A preliminary step is to put municipalities on notice of potential liability and to
16 inform their insurance carriers of potential liability. Insurance companies are not in the
17 business of defending unreasonable and known risks. They will begin to limit and
18 terminate coverage, and the foolish practice of water fluoridation will in many
19 municipalities be terminated.

20 B. APPLICANTS' FAMILIARITY WITH THE ISSUES AND ARGUMENT
21 PRESENTED BY THE PARTIES

22 An advisor to the Applicants has been following this case since the time it was
23 filed in superior court and has read all of the briefs filed in Superior Court, the Court of
MOTION TO FILE AMICUS CURIAE
BRIEF OF FLUORIDE CLASS ACTION - 2

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1
2 Appeals Division II, and the Supreme Court. Therefore the Applicants are well familiar
3 with the issues and arguments presented by the parties.

4 C. ISSUES TO WHICH THE AMICI CURIAE BRIEF WILL BE DIRECTED

5 The Amici Curiae Brief addresses Issues 2 and 5 presented in the Petition for
6 Review at 1-2.

7 D. APPLICANTS' REASON FOR BELIEVING THAT ADDITIONAL
8 ARGUMENT IS NECESSARY

9 If the Court of Appeals Division II ruling stands, it will effectively
10 disenfranchise local voters around the state of Washington from having the opportunity
11 to vote on these issues. Other states and other nations will follow the lead of
12 Washington State and this could lead to their citizens being disenfranchised as well.

13 For more than fifty years, local voters in this state, this nation, and around the
14 world have used local initiatives and referendums to vote on local public health
15 regulations to not have fluoridated water. The Opinion should not be allowed to end
16 local voters' right to continue to exercise police power to have local initiatives and
17 referendums to prohibit fluoridation and local voters should be allowed to prohibit or
18 limit other drugs as well.

19 This Amici Curiae Brief highlights some of the historical and economic facts
20 relating to the issue.
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Dated this 22nd day of January, 2010.

Respectfully submitted,

JAMES ROBERT DEAL PLLC

By:

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Attorney for Amici Fluoride Class Action

No. 82225-5

SUPREME COURT
OF THE STATE OF WASHINGTON

CITY OF PORT ANGELES, Respondent,
v.
OUR WATER-OUR CHOICE, and PROTECT OUR WATERS,
Petitioners,
v.
WASHINGTON DENTAL SERVICE FOUNDATION, LLC,
Respondent.

AMICUS CURIAE BRIEF OF FLUORIDE CLASS ACTION
IN SUPPORT OF PETITIONERS

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TABLE OF CONTENTS

I.	<u>IDENTITY AND INTEREST OF AMICUS CURIAE</u>	1
II.	<u>ISSUES ADDRESSED</u>	1
III.	<u>BRIEF STATEMENT OF THE CASE</u>	1
IV.	<u>THE COURT SHOULD LOOK AT THE SCIENCE</u>	1
IV.	<u>WHEN CITY WATER IS FLUORIDATED, RESIDENTS CANNOT AVOID ITS EFFECTS</u>	2
VI.	<u>IT IS HARD TO DETERMINE WHO HAS R ESPONSIBILITY REGARDING FLUORIDATION</u>	5
VII.	<u>WHERE DOES FLUORIDE COME FROM?</u>	15
VIII.	<u>WHY DO WE FLUORIDATE?</u>	17
XI.	<u>CONCLUSION</u>	20
	CERTIFICATE OF SERVICE	21

TABLE OF AUTHORITIES

Cases

- 1, 2 Kaul v. Chehalis, 45 Wn.2d 616, 277 P.2d 352 (1954)
- 2 Dev. Servs. V. City Of Seattle, 138 Wn.2d 107, 979 P.2d 387 (1999) at 120

RCW

- 12 RCW 42.56.080

WAC

- 12 WAC 246-290-220(3),
- 15 WAC 246-290-460

CFR

- 21-22 21 CFR 165.110; see 2006 NRC Report at
- 11 40 CFR 141.51

USC

- 5 21 U.S.C. sec. 321(g)(1)(B)
- 9 42 USC 300g-1(b)(11):

Other Documents

- 13 2006 NRC Report at 20
- 12, 15 February 2008 NSF Fact Sheet on Fluoridation Chemicals

- 22 Health Effects: Fluoride & the Kidneys,
www.FluorideAlert.org
- 10 July 7, 2000, letter from Stan Hazan, then NSF general
manager, to Rep. Ken Calvert
- 19 Lucier Chemical Industries invoice
- 9 Memorandum of Understanding, numbered MOU 225-79-
2001
- 13 October 28, 2008, letter from Gregg Grunenfelder of the
Department of health to Eloise Kailin
- 18 Rebecca Hanmer letter to Leslie Russell, 1983
- 14 Tudor Davies April 2, 1998, letter to George Glasser

Table of Appendices

A	Interest Statement of Fluoride Class Action
B-1	Purified Water, http://en.wikipedia.org/wiki/Purified_water
B-6	Appendix B-62006 NRC Report at 21-22
B-8	Price List, whole house reverse osmosis water system
B-10	Environmental Working Group Notes
B-12	Memorandum of Understanding, numbered MOU 225-79-2001
B-16	July 7, 2000, letter from Stan Hazan, then NSF general manager, to Rep. Ken Calvert
B-26	2006 NRC Report
B-27	February 2008 NSF Fact Sheet on Fluoridation Chemicals
B-35	40 CFR 141.51
B-43	Blake Stark response to a request for toxicological studies
B-44	Wikipedia article on Hexafluorosilicic acid
B-47	October 28, 2008, letter from Gregg Grunenfelder of the Department of health to Eloise Kailin
B-48	Tudor Davies April 2, 1998, letter to George Glasser
B-49	Bone Valley, an article from Wikipedia
B-58	Photos of fluoride ponds and sink holes
B-56	Phosphate Fertilizer Industry: An Environmental Overview, FluorideAlert.org
B-68	Phosphate Rich Organic Manure

B-69

Rebecca Hanmer letter to Leslie Russell, 1983

I. **IDENTITY AND INTEREST OF AMICUS I CURIAE**

Fluoride Class Action is an association that opposes using public water systems to medicate people. See the attached Appendix A for a statement of its interest in this case.

II. **ISSUES ADDRESSED**

This Amicus Curiae Brief addresses Issues 2 and 5 presented in the Petition for Review at 1-2.

III. **BRIEF STATEMENT OF THE CASE**

Fluoride Class Action adopts the Brief Statement of the Case in the Amici Curiae Brief of International Academy of Oral Medicine and others (“IAOMT Amici Brief”).

IV. **THE COURT SHOULD LOOK AT THE SCIENCE.**

The case of *Kaul v Chehalis*, 45 Wn.2d 616, 277 P.2d 352 (1954), is one example of how scientific facts can impact the outcome of a case. The Kaul court agreed with the trial court’s finding that fluoridation with sodium silicofluoride at 1 ppm was “wholesome,” that fluoridation was beneficial to some, particularly young children, and harmful to no one. Kaul at 621. The minority nevertheless made the argument that the insertion of medication into water violated individual liberty and the right of a person to control his/her own body. However, the minority argument

rang a little hollow because the dissenters were bound by the fact that all parties considered fluoride both harmless and beneficial. If the 2006 NRC Report¹ had been available in 1954, the decision might have been very different.

The Court requires that there be a necessary element which is “rationally related to” a “legitimate government purpose.” *Dev. Servs. V. City Of Seattle*, 138 Wn.2d 107, 979 P.2d 387 (1999) at 120. This means the cost and the benefit must be weighed. If there is little or no benefit to fluoridation and significant cost or harm to those who drink the water, then the fluoridation decision fails the test. Thus, the Court must take the relevant science into account. I will list some of the relevant scientific and legal-scientific facts, many of which the Court can take judicial notice.

I am certainly no Louis Brandeis, but in this brief I will try to give the Court a broader practical, historical, and economic view of the issues.

V. WHEN CITY WATER IS FLUORIDATED, RESIDENTS CANNOT AVOID ITS EFFECTS.

The Kaul Court, apparently quoting from the trial court’s findings stated: If the water is fluoridated, it will be necessary for appellant and all other users “to use it for domestic purposes including drinking, because there is no other practical source of supply.” *Id.* at 618. Contrast this with other medications or vitamins

¹ National Research Council, *Fluoride in Drinking Water: A Scientific Review of EPA’s Standards* (2006), referred to herein as the “2006 NRC Report”

which the federal government requires be added to food. By law, white and brown flour must be fortified with calcium, iron, thiamin and niacin. Both lowfat and nonfat milk must be fortified with vitamin A. Individuals can choose to drink whole milk instead of lowfat or nonfat milk, which does not have to be fortified, and they can choose to eat bread made with whole wheat flour, which does not have to be enriched. So a person can easily avoid consuming these additives. Despite the government mandate that these foods be “medicated” with vitamins he/she might not want to consume, he/she retains a real ability not to consume them.

However, avoiding the fluoride in tap water is not so easy. One must avoid drinking and cooking with tap water. One must buy either a distiller or a reverse osmosis filter. A cheap Brita filter will not remove the tiny fluoride ion. See Purified Water, http://en.wikipedia.org/wiki/Purified_water, attached as Appendix B-1. Or one must buy distilled or spring water at the at much greater cost than tap water. Water weighs 8 pounds per gallon, so the elderly, the frail, the impaired, and those who rely on public transit, will have a hard hauling the water home. Further, some bottled water contains fluoride, and labeling disclosure is not required unless fluoride in addition to fluoride which occurs naturally or is added by the city. See 21 CFR 165.110; see 2006 NRC Report at 21-22; see Appendix B-6. Or one can buy five gallon jugs and journey to an artesian well like the one

on 164th Street SW in Lynnwood, Washington, just to the west of I-5 and on the north side of the street, or visit a friend who receives non-fluoridated water.

Further, one who wants to avoid fluoride must avoid restaurant food and Starbucks coffee, which are presumably made with fluoridated water. One must also inquire as to whether his bread is baked and his beer is brewed and his pop is bottled with fluoridated water.

As covered in the amicus brief of Reverend Lynn Lohr, a small but real portion of the population is hypersensitive to fluoride, and some of them must even avoid taking a bath or shower in fluoridated tap water. Clothes are washed in fluoridated water, and the fluoride is left in the clothes after the water evaporates. As one perspires during the day, the fluoride in clothes will bathe the skin. To avoid these problems one must buy a whole-house reverse osmosis filter, which is expensive. Go to Google and search for “whole house reverse osmosis water system,” and see the attached price list labeled as Appendix B-8.

The point of this section is to make it clear that if one lives in a fluoridated city, it is hard to avoid fluoride, and this affects the constitutional calculation.

Further, there are sources of fluoride other than drinking water. The Environmental Working Group notes that there is up to 900 ppm of fluoride in dried eggs and that one-third of all eggs are dried and then added to food products. See Appendix B-10. Other foods may contain

substantial fluoride residues from the use of fluoride as a pesticides and fumigants.

VI. IT IS HARD TO DETERMINE WHO HAS RESPONSIBILITY REGARDING FLUORIDATION.

The Centers for Disease Control (CDC) is probably the biggest cheerleader for drinking water fluoridation in the United States. See <http://www.cdc.gov/fluoridation>. Surgeon Generals have endorsed drinking water fluoridation as well. However, neither the CDC nor the Surgeon General has any jurisdiction over water fluoridation whatsoever.

As discussed in the IAOMT Amici Curiae brief at 8-9, 12-13, and 16-18, the US Federal Drug Administration (FDA) should have jurisdiction over fluoride added to water, simply because fluoridated water meets the definition of a drug. The Food, Drug, and Cosmetics Act (FDCA) defines a drug as an article "... intended for use in the diagnosis, cure, mitigation, treatment, or prevention of disease in man or other animal. 21 U.S.C. 321 (g)(1)(B). Dental caries is a disease, and fluoride is added to water to prevent caries.

However, the FDA has not asserted jurisdiction over fluoride used to fluoridate tap water nor over the fluoride-tap water mixture called fluoridated water. The FDA has asserted jurisdiction over toothpaste and mouthwash, which are not to be swallowed, and has asserted limited

jurisdiction over fluoridated bottled water. But the FDA has not asserted jurisdiction over the fluoride-tap water drug.

A new section was added to the Safe Drinking Water Act (SDWA) in 1974 which specifically forbade the EPA from requiring the addition of fluoride to drinking water. The SDWA states at 42 USC 300g-1(b)(11):

No national primary drinking water regulation may require the addition of any substance for preventive health care purposes unrelated to contamination of drinking water.

However, the FDA and the EPA got together in 1979 and entered into an inter-agency treaty, a Memorandum of Understanding, numbered MOU 225-79-2001, labeled as Appendix B-12, in which the agencies agreed that the FDA would "... control bottled drinking water and water, and substances in water, used in food and for food processing ..." On the other hand, the EPA would

"... take appropriate measures, under the SDWA and/or TSCA [Toxic Substances Control Act], and FIFRA [Federal Insecticide, Fungicide, and Rodenticide Act], to control direct additives to drinking water (which encompass any substances purposely added to the water), and indirect additives (which encompass any substance which might leach from paints, coatings or other materials as an incidental result of drinking water contact), and other substances.

There were two problems with this deal. First only Congress can change a federal statute. Agencies cannot cede their authority to each other. Second, the FDA was ceding to the EPA all its authority "to control direct

additives to drinking water.” However, the EPA had been prohibited in 1974 from creating any regulations which require adding any “substance for preventive health care purposes unrelated to contamination of drinking water.” The FDA was ceding to the EPA a role it could legally not fill.

The net result was that neither agency was willing or legally capable of regulating the addition of fluoride to drinking water, although the illegal treaty made it appear that the EPA had been given such authority.

Next, in 1985 the EPA off-loaded authority it did not have to write regulations governing the addition of fluoride to drinking water to a trade association known as NSF International (NSF).

Who or what is NSF? I quote from Appendix B-16, a July 7, 2000, letter from Stan Hazan, then NSF general manager, to Rep. Ken Calvert:

NSF involvement in the evaluation of drinking water chemicals, including fluoride-based chemicals, began in 1985, when the U.S. EPA granted an NSF-led consortium of stakeholders the responsibility to develop consensus, health-based, quality specifications for drinking water treatment chemicals and drinking water system components (Attachment 1). EPA also requested development of a product testing and certification program that would allow for independent product evaluations for use by states, cities, and water utilities, as a basis for product acceptance and use. The original goal of the standard and certification program was to develop a preventative mechanism for selecting treatment chemicals that would not contribute harmful levels of contaminants to drinking water. ... The standards and the certification program were designed to be dynamic, to change as regulations change, and to constantly be tied to the requirements of the Safe Drinking

Water Act and its drinking water quality regulations. In 1988, EPA terminated its informal chemical additives advisory program upon completion of the NSF standards and successful launch of the NSF product certification program [emphasis added]... .

NSF proceeded to construct NSF Rule 60, which is the logo which is stamped on every fluoride shipment bill of lading.

NSF 60 Drinking water treatment chemicals – Health effects was initially adopted in December 1987, and was last revised in May 2000. It establishes minimum human health effects requirements for the chemicals that are added directly to drinking water for its treatment or other purposes. The standard was developed using a consensus standards development process with representation of the major stakeholder interests, including product manufacturers [emphasis added].... Id., Appendix B-20.

So the industries which produce hydrofluosilicic acid are on the board which developed it.

The letter contains contradictory statements regarding testing of the fluoride product:

The standard requires that the manufacturer of a product submitted for certification provide toxicological information, if available. NSF requires that manufacturers seeking certification to the standard submit this information as part of their formulation or ingredient supplier submission. ... Id., Appendix B-21.

However, the information submitted by the manufacturer is not available for the public to read:

Individual test reports, as well as formulation information are protected by nondisclosure agreements with certification clients. Id., Appendix B-21.

NSF took over fluoride regulation from the EPA but NSF Standard 60 is a private document. To read it you must buy it for \$325.

<http://www.techstreet.com/cgi-bin/results>. Do a Washington Request for Documents under the Public Records Act, RCW 42.56.080, addressed to a water district and ask for a copy of Standard 60. You will find out that the water districts do not even have a copy. So how can we have a WAC 246-290-220(3), which requires water districts to conform to a Standard 60 which most people and even most government officials have never seen?

Note that NSF follows the EPA 4 ppm Maximum Contaminant Level for fluoride:

NSF has based its certification on the product use not exceeding the EPA's MCL [maximum contaminant level] for fluoride. ... Contaminants in the finished drinking water are not permitted to exceed one-tenth of the EPA's regulated MCL (Maximum Contaminant Level) when the product is added to drinking water at its Maximum Use Level, unless it can be documented that a limited number of sources of the contaminant occur in drinking water. ... Hazen, Appendix B-21.

However, NSF does not follow its own rule. Instead of setting a .4 ppm MAL, maximum allowable level, which would be one-tenth of the EPA 4.0 ppm MCL, it sets a 1.2 ppm MAL:

An MAL of greater than 10% of the MCL can be established by the certification body in limited cases if it can be reasonably documented that there are no other significant sources of the same contaminant, that together, would result in the finished drinking water contaminant concentration exceeding the MCL. Fluoride has an MAL of 1.2 mg / liter, which is 30% of the MCL. This is

justified on the basis of the limited number of other potential sources of fluoride ion to drinking water. For example, water that naturally contains sufficient fluoride is not additionally fluoridated, and fluoride is seldom present in other additives. Id., Appendix B-16.

The justification given is that there are no other sources of fluoride to add to the 30 percent load. However, there are many other sources of fluoride besides the fluoride added to drinking water, the greatest being naturally occurring fluoride. See 2006 NRC Report at 20. Appendix B-26. Again, NSF violates its own rule.

More importantly, note that NSF is using the SDWA 4.0 ppm MCL to authorize adding fluoride to water. Remember that the SDWA cannot “require the addition of any substance for preventive health care purposes unrelated to contamination of drinking water.” The 4.0 ppm is not a license to add fluoride up to the 4.0 ppm level but a requirement to remove fluoride if the level exceeds 4.0 ppm. So the NSF is using the SDWA 4.0 ppm MCL to do something that the SDWA does not allow the EPA or the states as enforcers of the SDWA and perhaps even the municipalities as enforcers of the SDWA to do, that is to add fluoride to water. Maybe this shows that the people running the NSF do not understand what the SDWA did not allow.

So if the municipalities choose to fluoridate, they do it on their own, except that they are relying on the NSF for cover. In fact, Washington law, WAC 246-290-220(3), requires that

any treatment chemicals with the exception of commercially retailed hypochlorite compounds such as Clorex, Purex, etc., added to water intended for potable use must comply with ANSI/NSF Standard 60.

By law, municipalities must conform to a sham law. I am trying to think of another situation where a state law requires a municipality to follow rules set up by a trade association.

The February 2008 NSF Fact Sheet on Fluoridation Chemicals, Appendix B-27, contains more ironies. It says:

The NSF Joint Committee on Drinking Water Additives continues to review and maintain the standard annually. This committee consists of representatives from the original stakeholder groups as well as other regulatory, water utility and product manufacturing representatives. ... Standard 60 ... requires a toxicology review to determine that the product is safe at its maximum use level and to evaluate potential contaminations in the product. ... A toxicology evaluation of test results is required to determine if any contaminant concentrations have the potential to cause adverse human health effects. ... NSF also requires annual testing and toxicological evaluation of each NSF Certified product. NSF Certified products have the NSF Mark ... on the product packaging ... shipped with the product. The NSF standard requires that the treatment products added to drinking water, as well as any impurities in the products are supported by toxicological evaluation. ... [F]luosilicic acid is produced by adding sulfuric acid to phosphate ore. This is typically done during the production of phosphate additives for agricultural fertilizers. ... The most common contaminant detected in these products is arsenic The current MCL for arsenic is 10 ppb, the highest detection of arsenic

from a fluoridation chemical was 0.6 ppb The third most common contaminant found is lead ... with 0.6 ppb being the highest concentration detected [emphasis added].

However, the MCLG, the maximum contaminant level goal, for arsenic and lead are both zero. See 40 CFR 141.51, Appendix B-35. These chemicals are so nasty that there is no justification for adding any of them to drinking water. See Wikipedia article on Arsenic, Appendix B-36. Fluoride is a little more toxic than lead, a little less toxic than arsenic. However, the MCL for lead is 15 ppb; the MCL for arsenic is 10 ppb; but the MCL for fluoride is 4,000 ppb, that is 4.0 ppm. See Appendix B-42, Clin Toxicology Commer Products. In the next section of this brief I will discuss how it has happened that we are adding these three toxic elements to our water and why we add so much more fluoride than the others.

If there is any doubt regarding the bogus nature of NSF Standard 60 certification, read through the NSF documents again looking for any reference to the results of the 2006 NRC Report. There is none. NSF standards are outdated. Look through the NSF web site at www.NSF.org for any toxicological studies. You will find none.

Blake Stark is the person at NSF International now in charge of fielding questions regarding Standard 60. I talk with Blake from time to time. His contact information is: 734-769-5480, Stark@NSF.org. Call him or e-mail him and ask him if NSF has any toxicological studies on

hydrofluosilicic acid. He will answer and talk with you. See an example of a Blake Stark response to a request for toxicological studies, labeled as Appendix B-43.

Note that the February 2008 NSF Fact Sheet on Fluoridation Chemicals discusses “fluosilicic acid.” Fluosilicic acid and hexafluorosilicic acid are the same thing as fluosilicic acid. See Wikipedia article on Hexafluorosilicic acid, Appendix B-44. Note also that it is “fluorosilicic acid which Port Angeles is adding to city water.” See the October 28, 2008, letter from Gregg Grunenfelder of the Department of health to Eloise Kailin, Appendix B-47. Mr. Grunenfelder says:

[W]e rely on national certification protocols to ensure the safety of water additives. Specifically, Washington Administrative Code 246-290-220(3), requires that: “Any treatment chemicals ... must comply with ANSI/NSF Standard 60.... Since the fluoridation product being used by the city of Port Angeles is certified under NSF Standard 60, the city’s use of this product is in compliance with state law.

So this is how the shell game works. Most people naively assume that the EPA has jurisdiction over drinking water fluoridation through the SDWA. The EPA helped start NSF and gave it legitimacy. The NSF pretends to be authoritative, and so people trust it when its fact sheet mentions health and safety, inspections, and toxicology. What is going on is that the NSF is

pretending to do what the EPA by law was unable to do, to regulate the addition of fluoride to water.

Remember, as I explained in the Adams- Martin amicus brief at 15-16, the EPA 4 ppm limit is not an authorization to add fluoride up to 4 ppm, but a requirement that if fluoride occurs naturally or perhaps through pollution at greater than 4 ppm it must be removed. The SDWA, enforced by the EPA, authorizes adding chemicals, but only those which will remove contaminants.

Water commissioners like Grunenfelder are deceived by the shell game. This is a different kind of shell game. In the old days there was a pea under one of the walnut shells. In this case, there is no pea under any of the shells.

Tudor Davies, former director of the Office of Science and Technology for the EPA stated in his April 2, 1998, letter to George Glasser, Appendix B-48, the following:

In the United States, there are no Federal safety standards which are applicable to drinking water additive, including those intended for use in fluoridating water. In the past the EPA assisted the States and public water systems through the issuance of advisory opinions on acceptability of many additive chemicals. However, the Federal advisory program was terminated on October 4, 1988, and EPA assisted in establishment of voluntary product standards at NSF International (NSF) NSF Standard 60 ... was developed by NSF by a consortium of representatives from utilities, government, manufacturers and the public health community.

No federal agency is empowered to write regulations which require that fluoride be added to drinking water, so we must ask if there is a Washington agency which does so? The Department of Health is the lead agency for enforcement of the SDWA in Washington, but it is forbidden by the SDWA from writing a regulation requiring the addition to water of “any substance for preventive health care purposes unrelated to contamination of drinking water.” See the Adams-Martin amicus brief at 14-15. Further, the Department of Health does not require the addition of fluoride to water, it merely says that if a municipality fluoridates, it must follow certain fluoridation practices. WAC 246-290-460. The municipalities make the decision to fluoridate.

VII. WHERE DOES FLUORIDE COME FROM?

As noted above Gregg Grunenfelder of the Department of Health said that the fluoride added to Port Angeles water is fluorsilicic acid. Recall that the February 2008 NSF Fact Sheet on Fluoridation Chemicals mentioned above, says that fluorsilicic is generally produced by adding sulfuric acid to phosphate ore to make fertilizer.

Fluoride can come from aluminum and steel plants, where it is used as a flux to lower the melting point of the metal. It is used in great quantity to produce uranium because fluorine dissolves uranium to produce uranium hexafluoride. However, since the end of World War II,

by far the biggest source of fluoride has been the production of super-phosphate fertilizer.

In order to produce phosphorus that can be quickly absorbed by plants, raw phosphate ore must be processed to produce commercial phosphate fertilizer. Phosphate ore contains heavy metals such as lead and uranium as well as arsenic and is around 4% fluoride. Sulfuric acid is added to the ore. Fluoride gasses are produced. In the past the gasses were vented up the smokestack, and entire counties were poisoned by the fluoride fumes. Today the fumes must pass through a scrubber liquor, which captures most of the fluoride along with the heavy metals. The raw scrubber liquor is put in tankers with no filtration or any further processing and shipped to thousands of water districts around the world, including Port Angeles.

Common fluoride is the unprocessed slurry liquor left over after phosphate fertilizer, aluminum, steel, or uranium is produced. It is filth. Although it is diluted 180,000 times, it is still filth.

The phosphate fertilizer industry is itself a pollution nightmare. In addition to producing millions of gallons of fluoride, it also yields millions of tons of useless left over "gypsum." Gypsum is mostly silicon. This pretty white small gravel gypsum would be perfect for building roadbed foundations, but unfortunately it is radioactive. So it is dredged from

fluoride cooling ponds and stacked in gigantic piles a hundred feet high which surround the ponds and extend over areas the size of cities. There it will probably remain for all eternity. The EPA accepts indefinite disposal onsite. There is probably nothing that could be done with this waste. See the attached Appendix B-49 entitled Bone Valley, an article from Wikipedia describing one region where phosphate fertilizer and fluoride are produced.

Unfortunately, a sink hole opened up under a gypsum pile in Florida, and thousands of tons of gypsum fell into the Florida aquifer, permanently polluting the river of water that runs under the state. See photos attached and labeled as Appendix B-54. See Phosphate Fertilizer Industry: An Environmental Overview, Appendix B-56 for more scandalous information about the phosphate fertilizer industry. For a satellite's eye view of wreckage in another area go to <http://maps.google.com> and do a search for "Purvis Still White Springs Florida." Click on "satellite" view.

Further clarifying the enormity of this tragedy is the simple fact that the superphosphate fertilizer industry is unnecessary. Its product is designed for quick results and growing corn, wheat, and cotton as fast as possible. The problem with superphosphate fertilizer is that it builds up in the soil and deadens microbial life in the soil. Organic farmers use

ordinary ground up rock phosphate which they compost in animal or plant manure. It takes more time and is more work, but the end result is healthier soil and healthier plants. See Phosphate Rich Organic Manure, Appendix B-68.

VIII. WHY DO WE FLUORIDATE?

Christopher Bryson describes how it came about in his masterful book *The Fluoride Deception*. Just as there were captains of industry and public relations experts who convinced us that cigarettes, asbestos, tetraethyl lead, and DDT were good for us, there were leaders in the aluminum industry who believed that naturally occurring calcium fluoride reduced caries but who also had excess fluoride to sell. The Mellon Institute, which had promoted asbestos and tetraethyl lead, although knowing they were harmful long before they were outlawed, promoted fluoride fraudulently. Edward Bernays, nephew of Sigmund Freud, probably the first true public relations expert, the man who convinced women to take up cigarette smoking, also promoted drinking water fluoridation, in league with the National Institute of Dental Research. There was a lot of toxic fluoride waste to get rid of, and there was money to be made. Rebecca Hanmer, EPA official, stated in 1983:

In regard to the use of fluosilicic acid as a source of fluoride for fluoridation, this agency regards such use as an ideal environmental solution to a long-standing problem. By recovering

by-product fluosilicic acid from fertilizer manufacturing, water and air pollution are minimized, and water utilities have a low-cost source of fluoride. Rebecca Hanmer letter to Leslie Russell, 1983, See Appendix B-69.

Port Angeles pays around \$520 per ton for this fraudulent chemical. See Appendix B-70, a Lucier Chemical Industries invoice for a 12 ton load that cost the City \$6,214. Fluoride producers turn a waste product into a profit center. One estimate is that 200,000 tons of fluoride is sold yearly for drinking water fluoridation. That adds up to a \$104 million per year industry. Fluoride promoters made large donations to dental schools, and certain dentists became their best lieutenants. (Scholarly dentists are among fluoridation's most active opponents.)

And it is a fact that people do sometimes believe in lies. For centuries the majority believed slavery was God's will, that women were inferior, and that Jews were evil. Our faith in fluoridation has been persistent. Opposition to fluoridation has been muted because fluoridation opponents, under pressure from the pro-fluoridation lobby, have been denied research funding, driven from academic positions, and lampooned as kooks. Back in the 1950s the John Birch Society opposed fluoridation as a communist conspiracy. The Birchers were derided as paranoid conspiracy theorists, and scientific opponents were classed with the Birchers and thus marginalized. The Birchers were wrong: Fluoride is not

a communist conspiracy; it is an aluminum, steel, uranium and fertilizer conspiracy.

IX. **CONCLUSION**

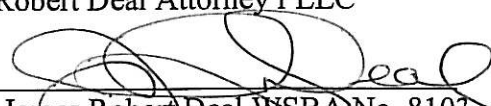
Fluoride Class Action requests that this Court allow the Initiatives to be put on the ballot in Port Angeles so the citizens can decide if they want to have their public water supplies free of fluoride and other drugs.

Dated this 22nd day of January, 2010.

Respectfully submitted,

James Robert Deal Attorney PLLC

By: _____


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CERTIFICATE OF SERVICE

I certify that on the 22nd day of January, 2010, I caused a true and correct copy of this certificate and the Amicus Curiae Brief of Washington Action for Safe Water In Support of Petitioners and Motion to File Amici Curiae Brief to be served on the following as follows:

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James Robert Deal

APPENDIX A
STATEMENT OF INTEREST
FLUORIDE CLASS ACTION

The work of Fluoride Class Action may be viewed by going to the following web site: <http://fluoride-class-action.com>. It is the aim of Fluoride Class Action inspire class action and consumer protection attorneys to sue municipalities which deliver fluoridated water for harm done to those who consume the water. The aim is to serve as a repository of information about how to proceed with these cases and to make this information available to fellow attorneys.

A healthy person stores half of all fluoride ingested mostly in his/her bones, while the person with kidney disease retains 80%, and it is a downward spiral for him/her. See Appendix B-71, Health Effects: Fluoride & the Kidneys, www.FluorideAlert.org. To make a successful case against municipalities it is not necessary to prove that fluoride is the only cause of harms; it is only necessary to prove that fluoride exacerbates health problems and hastens death. For example, the lifespan of any person who died of kidney disease at an early age was probably shortened by consumption of fluoride.

A preliminary step is to put municipalities on notice of potential liability and to inform their insurance carriers of potential liability. Insurance companies are not in the business of defending unreasonable

and known risks. They will begin to limit and terminate coverage, and the foolish practice of water fluoridation will in many municipalities be terminated.

Purified water

From Wikipedia, the free encyclopedia

Purified water is water from any source that is physically processed to remove impurities. Distilled water and **deionized water** have been the most common forms of purified water, but water can also be purified by other processes including reverse osmosis, carbon filtration, microporous filtration, ultrafiltration, ultraviolet oxidation, or electrodialysis. In recent decades, a combination of the above processes have come into use to produce water of such high purity that its trace contaminants are measured in parts per billion (ppb) or parts per trillion (ppt). Purified water has many uses, largely in science and engineering laboratories and industries, and is produced in a range of purities.

Contents

- 1 Methods of purifying water
 - 1.1 Distillation
 - 1.2 Double-distillation
 - 1.3 Deionization
 - 1.4 Other processes
- 2 Uses
 - 2.1 Laboratory use
 - 2.2 Non-laboratory uses
- 3 Health effects
- 4 See also
- 5 References



Bottle for Distilled water in the Real Farmacia in Madrid

Methods of purifying water

Distillation

Main article: Distilled water

Distilled water is often defined as bottled water that has been produced by a process of distillation and has an electrical conductivity of not more than 10 $\mu\text{S}/\text{cm}$ and total dissolved solids of less than 10 mg/L ^[1]. Distillation involves boiling the water and then condensing the steam into a clean container, leaving most solid contaminants behind. Distillation produces very pure water but also leaves behind a leftover white or yellowish mineral scale on the distillation apparatus, which requires that the apparatus be frequently cleaned.^[*expand*] Distillation does not guarantee the absence of bacteria in drinking water; unless the reservoir and/or bottle are sterilized before being filled, and once the bottle has been opened, there is a risk of presence of bacteria

For many applications, cheaper alternatives such as deionized water are used in place of distilled water.

Double-distillation

Double-distilled water (abbreviated " ddH_2O ", "Bidest. water" or "DDW") is prepared by double distillation of water. Historically, it was the de facto standard for highly purified laboratory water for biochemistry and trace analysis until combination methods of purification became widespread.

Deionization

Deionized water, also known as *demineralized water*^[2] (*DI water*, *DIW* or *de-ionized water*; can also be spelled *deionised water*, see *Spelling differences*), is water that has had its mineral ions removed, such as cations from sodium, calcium, iron, copper and anions such as chloride and bromide. Deionization is a physical process which uses specially-manufactured ion exchange resins which bind to and filter out the mineral salts from water. Because the majority of water impurities are dissolved salts, deionization produces a high purity water that is generally similar to distilled water, and this process is quick and without scale buildup. However, deionization does not significantly remove uncharged organic molecules, viruses or bacteria, except by incidental trapping in the resin. Specially made strong base anion resins can remove Gram-negative bacteria. Deionization can be

done continuously and inexpensively using electrodeionization.

Deionization does not remove the hydroxide or hydronium ions from water. These are the products of the self-ionization of water to equilibrium and therefore are impossible to remove.

Other processes

Other processes are also used to purify water, including reverse osmosis, carbon filtration, microporous filtration, ultrafiltration, ultraviolet oxidation, or electrodialysis. These are used in place of, or in addition to the processes listed above.

Uses

Laboratory use

Water quality "norms" for purified water have been established by a number of professional organizations, including the American Chemical Society (ACS), the American Society for Testing and Materials (ASTM), the National Committee for Clinical Laboratory Standards (NCCLS) which is now CLSI, and the U.S. Pharmacopeia (USP). The ASTM, NCCLS, and ISO 3696 classify purified water into Grade 1-3 or Types I-IV depending upon the level of purity. These organizations have similar, although not identical parameters for highly purified water.

Regardless of which organization's water quality norm is used, even Type I water may require further purification depending upon the specific laboratory application. For example, water that is being used for molecular biology experiments needs to be DNase or RNase-free, which requires special additional treatment or functional testing. Water for microbiology experiments needs to be completely sterile, which is usually accomplished by autoclaving. Water used to analyze trace metals may require elimination of trace metals to a standard beyond that of the Type I water norm.

Maximum Contaminant Levels in Highly Purified Water^[3]

Contaminant	Parameter	ISO 3696 (1987)			ASTM (D1193-91)				NCCLS (1988)			Pharmacopoeia	
		Grade 1	Grade 2	Grade 3	Type I*	Type II**	Type III***	Type IV	Type I	Type II	Type III	EP	USP
Ions	Resistivity at 25 °C/MO•cm	10	1	0.2	18.0	1.0	4.0	0.2	>10	>1	>0.1	>0.23	>0.77
	Conductivity at 25 °C/μS•cm ⁻¹	0.1	1.0	5.0	0.056	1.0	0.25	5.0	<0.1	<1	<10	<4.3	<1.3
Acidity/Alkalinity	pH at 25 °C	-	-	5.0–7.5	-	-	-	5.0–8.0	-	-	5.0–8.0	-	-
Organics	Total Organic Content/p.p.b.	-	-	-	100	50	200	-	<50	<200	<1000	<500	<500
Total Solids	mg/kg	-	1	2	-	-	-	-	0.1	1	5	-	-
Colloids	Silica/μg/mL	-	-	-	<3	<3	<500	-	<0.05	<0.1	<1	-	-
Bacteria	CFU/mL	-	-	-	-	-	-	-	<10	<1000	-	<100	<100

Conductivity of ultra-pure water is $5.5 \times 10^{-6} \text{ S}\cdot\text{m}^{-1}$ (18 MO cm) and is due only to H^+ and OH^- ions produced in the water dissociation equilibrium.^[4] This low conductivity is only achieved, however, in the presence of dissolved monoatomic gases. Completely de-gassed ultra-pure water has conductivity of $1.2 \times 10^{-4} \text{ S}\cdot\text{m}^{-1}$, whereas upon equilibration to the atmosphere it is $7.5 \times 10^{-5} \text{ S}\cdot\text{m}$ due to dissolved CO_2 in it.^[4] The highest grades of ultrapure water should not be stored in glass or plastic containers because these container materials leach (release) contaminants at very low concentrations. Storage vessels made of silica are used for less demanding applications and vessels of ultrapure tin are used for the highest purity applications.

An example of a laboratory quality source is Milli-Q which is used in several analytical geochemistry and biological laboratories.

Non-laboratory uses

Distilled or deionized water are commonly used to top up lead acid batteries used in cars and trucks. The presence of foreign ions commonly found in tap water will cause a drastic reduction in an automobile's battery lifespan.

Distilled or deionized water is preferable to tap water for use in automotive cooling systems.^[5] The minerals and ions typically found in tap water can be corrosive to internal engine components, and can cause a more rapid depletion of the anti-corrosion additives found in most antifreeze formulations.^{[6][7]} Distilled or deionized water is especially important in automotive hybrid system component cooling systems, mixed with hybrid system coolant, to prevent corrosion and/or electrolysis of hybrid components.^[8]

Using distilled water in steam irons for pressing clothes, as well as other appliances such as humidifiers and cigar humidors which boil water, can reduce mineral scale build-up and help the appliance last longer. However, many iron manufacturers say that distilled water is no longer necessary in their irons.^{[9][10][11]}

For treatment of sleep apnea, patients using CPAP machines that have a humidifier are instructed to use distilled water so they do not inhale any impurities from non-purified water.

Purified water is used in freshwater and marine aquaria. Since it does not contain impurities such as copper and chlorine, it keeps fish free from diseases, as well as avoiding the build-up of algae on aquarium plants, due to its lack of phosphate and silicate. Deionized water should be re-mineralized before used in aquaria, since it also lacks many macro and micro-nutrients needed by both plants and fish.

Water (sometimes mixed with methanol) has been used to extend performance of aircraft engines. In piston engines it acts to delay the onset of detonation. In turbine engines it allows for more fuel flow for a given turbine temperature limit, and increases mass flow. As an example, it was used on early Boeing 707 models.^[12] Advanced materials and engineering have since rendered such systems obsolete for new designs.

Deionized water is very often used as an "ingredient" in many cosmetics and pharmaceuticals where it is sometimes referred to as "aqua" on product ingredient labels; see International Nomenclature of Cosmetic Ingredients. This use again owes to its lack of potential for causing undesired chemical reactions due to impurities.

Because of its high relative dielectric constant (~80), deionized water is also used (for short durations) as a high voltage dielectric in many pulsed power applications, such as Sandia National Laboratories' Z Machine.

Distilled water (such as *Wilkin's* distilled drinking water or *Absolute* distilled water) can also be used in PC watercooling systems and Laser Marking Systems. The lack of impurity in the water means that the system stays clean and prevents a build up of bacteria and algae. Also, the low conductance leads to less risk of electrical damage in the event of a leak or spillage. This enables the machine to work at optimal efficiency even after extensive periods of time without water exchange.

A recent use of purified water is that of a final rinse in some car washes where, because it contains no dissolved solutes, the car dries without leaving any spots. Another use of deionized water is in window cleaning, where window cleaners use pumped systems to brush and rinse windows with deionized water again without leaving any spots.

Deionized water has also recently found a use in an up to date version of water fog fire extinguishing systems. Such systems have been used in sensitive environments such as where high voltage electrical and sensitive electronic equipment is used. The 'sprinkler' nozzles use much finer spray jets and operate at up to 35 MPa (350 bar; 5000 psi) of pressure. The extremely fine mist produced takes the heat out of a fire rapidly and the deionized water coupled with the fine droplets is non conducting (when deionized) and may not damage sensitive equipment, not already damaged by fire. Deionized water, however, is inherently acidic and contaminants such as copper, dust, stainless and carbon steel and many other common materials rapidly supply ions thus re-ionizing deionized water. The very lack of ions make deionized water unusually corrosive and one of the most aggressive solvents known. It is not generally considered acceptable to spray water on electronic circuits that are in use or with power applied. It is wise to avoid mixing water and electricity.^{[13][14][15][16]}

Health effects

Distillation removes all minerals from water, and the membrane methods of reverse osmosis and nanofiltration remove most to all minerals. This results in demineralized water which is not considered ideal drinking water. The World Health Organization investigated the health effects of demineralized water in 1980, and its experiments in humans found that demineralized water increased diuresis and the elimination of electrolytes, with decreased serum potassium concentration. Magnesium, calcium, fluoride, and other nutrients in water can help to protect against nutritional deficiency. Demineralized water may also increase the risk from toxic metals because it more readily absorbs them, and because the presence of calcium and magnesium in water can prevent absorption of lead and cadmium. Recommendations for magnesium have been put at a minimum of 10 mg/L with 20–30 mg/L optimum; for calcium a 20 mg/L minimum and a 40–80 mg/L optimum, and a total water hardness (adding magnesium and calcium) of 2–4 mmol/L. At water hardness above 5 mmol/L, higher incidence of gallstones, kidney stones, urinary stones, arthrosis, and arthropathies have been observed. For fluoride the concentration recommended for dental health is

0.5–1.0 mg/L, with a maximum guideline value of 1.5 mg/L to avoid dental fluorosis.^[17]

Water filtration devices are becoming increasingly common in households. Most of these devices do not distill water, though there continues to be an increase in consumer-oriented water distillers and reverse osmosis machines being sold and used. Municipal water supplies often add or have trace impurities at levels which are regulated to be safe for consumption. Much of these additional impurities, such as volatile organic compounds, fluoride, and an estimated 75,000+ other chemical compounds^{[18][19][20]} are not removed through conventional filtration; however, distillation and reverse osmosis eliminate nearly all of these impurities.

The drinking of purified water has been both advocated and discouraged for health reasons. Purified water lacks minerals and ions, such as calcium, which are normally found in potable (drinking) water, and which have important biological functions such as in nervous system homeostasis. Some percentage of our daily consumption of these minerals and ions come from our drinking water, but most of them come from the food we eat, making DI water perfectly fine to drink if one has food in his or her system. The lack of naturally-occurring minerals in distilled water has raised some concerns. The Journal of General Internal Medicine^[21] published a study on the mineral contents of different waters available in the US. The study found that "drinking water sources available to North Americans may contain high levels of calcium, magnesium, and sodium and may provide clinically important portions of the recommended dietary intake of these minerals". It encouraged individuals to "check the mineral content of their drinking water, whether tap or bottled, and choose water most appropriate for their needs". Since distilled water is devoid of minerals, supplemental mineral intake through diet is needed to maintain proper health.

The consumption of "hard" water (water with minerals) is associated with beneficial cardiovascular effects. As noted in the American Journal of Epidemiology, consumption of hard drinking water is negatively correlated with atherosclerotic heart disease.^[22] Since distilled water is free of minerals, it will not have these potential benefits.

Some water is purified to avoid water fluoridation, which is the controlled addition of fluoride to a public water supply to reduce tooth decay. Although health and dental organizations worldwide have endorsed fluoridation's safety and effectiveness, opposition to water fluoridation is considerable, based on ethical, legal, safety, and efficacy grounds, and companies selling water filters are involved in the opposition.^[23] Whether purified water contains fluoride depends on which technology is used to purify the water. Pitcher or faucet-mounted filters do not alter fluoride; the more-expensive reverse osmosis filters remove 65%–95% of fluoride, and distillation filters remove all fluoride. Unnecessary use of filtered water may harm dental health.^[24]

See also

- Hydrogen production
- Ionized water
- Water ionizer
- Electrodeionization
- Atmospheric water generator (*Make distilled water from air*)
- Heavy water
- Water softening

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concentrations equal to or exceeding 4.0 mg/L.² Water supplies that exceeded 4.0 mg/L ranged as high as 11.2 mg/L in Colorado, 12.0 mg/L in Oklahoma, 13.0 mg/L in New Mexico, and 15.9 mg/L in Idaho (see Appendix B, Table B-3).³ States with the largest populations receiving water supplies with fluoride at ≥ 4.0 mg/L included Virginia (18,726 persons, up to 6.3 mg/L), Oklahoma (18,895 persons, up to 12.0 mg/L), Texas (36,863 persons, up to 8.8 mg/L), and South Carolina (105,618 persons, up to 5.9 mg/L).

Little information is available on the fluoride content of private water sources, but the variability can reasonably be expected to be high and to depend on the region of the country. Fluoride measured in well water in one study in Iowa ranged from 0.06 to 7.22 mg/L (mean, 0.45 mg/L); home-filtered well water contained 0.02-1.00 mg/L (mean, 0.32 mg/L; Van Winkle et al. 1995). Hudak (1999) determined median fluoride concentrations for 237 of 254 Texas counties (values were not determined for counties with fewer than five observations). Of the 237 counties, 84 have median groundwater fluoride concentrations exceeding 1 mg/L; of these, 25 counties exceed 2 mg/L and five exceed 4 mg/L. Residents in these areas (or similar areas in other states) who use groundwater from private wells are likely to exceed current guidelines for fluoride intake.

Duperon et al. (1995) pointed out that fluoride concentrations reported by local water suppliers can be substantially different from concentrations measured in water samples obtained in homes. Use of home water filtration or purification systems can reduce the fluoride concentration in community water by 13% to 99%, depending on the type of system (Duperon et al. 1995; Van Winkle et al. 1995; Jobson et al. 2000). Distillation or reverse osmosis can remove nearly all the fluoride. The extent of use of home water filtration or purification systems nationally is not known but obviously would affect the fluoride intake for people using such systems. Van Winkle et al. (1995) reported that 11% of their study population (in Iowa) used some type of home filtration either for well water or for public water.

Fluoride concentrations in bottled water⁴ are regulated by law to a maximum of 1.4-2.4 mg/L if no fluoride is added and a maximum of 0.8-1.7 mg/L if fluoride is added (the applicable value within the range depends on the annual average of maximum daily air temperatures at the location of retail sale; 21CFR 165.110[2003]). Maximum fluoride concentrations for imported bottled water are 1.4 mg/L if no fluoride is added and 0.8 mg/L if fluoride is added (21CFR 165.110[2003]). Fluoride concentrations are required on labels in the United States only if fluoride is added. Fluoride concentrations listed on labels or in chemical analyses available on the Internet for various brands range from 0 to 3.6 mg/L (Bartels et al. 2000; Johnson and

²More recently (2000), CDC has estimated that 850,000 people are served by public water supplies containing fluoride in excess of 2 mg/L; of these, 152,000 people receive water containing fluoride in excess of 4 mg/L (unpublished data from CDC as reported in EPA 2003c. Based on analytical data from 16 states, EPA (2003c) estimates that 1.5-3.3 million people nationally are served by public water supplies with fluoride concentrations exceeding 2 mg/L; of these 118,000-301,000 people receive water with fluoride concentrations greater than 4 mg/L.

³High-fluoride municipal waters are generally found in regions that have high fluoride concentrations in the groundwater or in surface waters. ATSDR (2003) has reviewed fluoride concentrations in environmental media, including groundwater and surface water. Fleischer (1962) and Fleischer et al. (1974) reported fluoride concentrations in groundwater by county for the coterminous United States.

⁴The term "bottled water" applies to water intended for human consumption, containing no added ingredients besides fluoride or appropriate antimicrobial agents; the regulations apply to bottled water, drinking water, artesian water, artesian well water, groundwater, mineral water, purified water, demineralized water, deionized water, distilled water, reverse osmosis water, purified drinking water, demineralized drinking water, deionized drinking water, distilled drinking water, reverse osmosis drinking water, sparkling water, spring water, and well water (21CFR 165.110[2003]).

DeBiase 2003; Bottled Water Web 2004); of those without added fluoride, most are below 0.6 mg/L. Most brands appear to list fluoride content only if they are specifically advertising the fact that their water is fluoridated; fluoride concentrations of these brands range from 0.5 to 0.8 mg/L (for "nursery" or "infant" water) up to 1.0 mg/L. Several reports indicate that fluoride concentrations obtained from the manufacturer or stated on labels for bottled waters might not be accurate (Weinberger 1991; Toumba et al. 1994; Bartels et al. 2000; Lalumandier and Ayers 2000; Johnson and DeBiase 2003; Zohouri et al. 2003).

Measured fluoride concentrations in bottled water sold in the United States have varied from 0 to 1.36 mg/L (Nowak and Nowak 1989; Chan et al. 1990; Stannard et al. 1990; Van Winkle et al. 1995; Bartels et al. 2000; Lalumandier and Ayers 2000; Johnson and DeBiase 2003). Van Winkle et al. (1995) reported a mean of 0.18 mg/L for 78 commercial bottled waters in Iowa. Johnson and DeBiase (2003) more recently reported values ranging from 0 to 1.2 mg/L for 65 bottled waters purchased in West Virginia, with 57 brands having values below 0.6 mg/L. Measured fluoride concentrations in bottled waters in other countries have similar ranges: 0.05-4.8 mg/L in Canada (Weinberger 1991), 0.10-0.80 mg/L in the United Kingdom (Toumba et al. 1994), and 0.01-0.37 mg/L more recently in the United Kingdom (Zohouri et al. 2003).⁵ Bartels et al. (2000) found significant variation in fluoride concentrations among samples of the same brand with different bottling dates purchased in the same city. In general, distilled and purified (reverse osmosis) waters contain very low concentrations of fluoride; drinking water (often from a municipal tap) and spring water vary with their source, as do mineral waters, which can be very low or very high in fluoride. Most spring water sold in the United States probably has a low fluoride content (<0.3 mg/L). Typical fluoride concentrations in various types of drinking water in the United States are summarized in Table 2-1.

TABLE 2-1 Typical Fluoride Concentrations of Major Types of Drinking Water in the United States

Source	Range, mg/L ^a
Municipal water (fluoridated)	0.7-1.2
Municipal water (naturally fluoridated)	0.7-4.0+
Municipal water (nonfluoridated)	<0.7
Well water	0-7+
Bottled water from municipal source	0-1.2
Spring water	0-1.4 (usually <0.3)
Bottled "infant" or "nursery" water	0.5-0.8
Bottled water with added fluoride ^b	0.8-1.0
Distilled or purified water	<0.15

^aSee text for relevant references.

^bOther than "infant" or "nursery" water.

⁵The European Commission has set a maximum limit of 5.0 mg/L for fluoride in natural mineral waters, effective January 1, 2008 (EC 2003). In addition, natural mineral waters with a fluoride concentration exceeding 1.5 mg/L must be labeled with the words "contains more than 1.5 mg/l of fluoride: not suitable for regular consumption by infants and children under 7 years of age," and for all natural mineral waters, the actual fluoride content is to be listed on the label. England has essentially the same requirements (TSO 2004), applicable to all bottled waters (natural mineral waters, spring water, and bottled drinking water).

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Public health bodies slam new fluoride tolerance levels

FoodNavigator-USA.com, Anthony Fletcher
Published October 2, 2005

Environmental organizations claim that new food tolerances for the fluoride-based pesticide sulfuryl fluoride could be potentially damaging to public health.

The new Environmental Protection Agency (EPA) tolerances were requested by Dow AgroSciences following the firm's expansion of its pesticide sulfuryl fluoride - trade name ProFume - which is used to fumigate food processing facilities and storage areas.

The product targets stored product pests, as well as those insects that may be transported from the field on food commodities. But some environmental groups argue that the new levels are potentially dangerous.

Indeed, the Environmental Working Group, Beyond Pesticides and the Fluoride Action Network (FAN) said that the maximum legal limits for the fluoride-based pesticide in foods have been set at levels that dwarf the amount allowed in tap water.

For example, the EPA is allowing 900 parts per million (ppm) of fluoride in dried eggs, as opposed to the maximum 4 ppm allowed in tap water. One third of the nation's eggs are sold and consumed in dried, reconstituted form.

The groups also noted that 900 ppm set for dried eggs is extremely close to that used in toothpaste (1,000 ppm), a level that is considered toxic if consumed in greater than pea sized portions.

"How can the EPA consider 900 ppm in eggs safe, while the Food and Drug Administration directs parents to call poison control centers if their

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children consume more than a pea sized portion of toothpaste with fluoride at 1,000 ppm?" asked Paul Connett, executive director of FAN.

"Unlike toothpaste, eggs are meant to be eaten, not spat out."

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It isn't just powdered eggs that could contain dangerous but legal levels of fluoride under the new regime. Fluoride Action Network (FAN) researcher Chris Neurath claims that all processed foods will be allowed 70 ppm fluoride residues, including everything from breakfast cereal to cake mix.

"Wheat flour is allowed up to 125 ppm," he said. "For comparison, the maximum level of fluoride allowed in drinking water is 4 ppm and the natural level of fluoride in mothers' milk is approximately 0.008 ppm. The potential for a significant number of acute poisoning cases every year is very real."

Dow AgroSciences however believes that the establishment of new accepted fluoride levels is great news for millers and food processors. "With the label amendments and additional tolerances, ProFume brings unprecedented flexibility and effective, reliable control of stored product pests to more markets segments and broadens its use pattern," said Drew Ratterman, marketing specialist, Dow AgroSciences.

"We appreciate the continued support of many throughout the industry during this registration process and are pleased to be able to offer a product that meets their fumigation needs."

However Richard Wiles, senior vice-president of the Environmental Working Group (EWG), contends that EPA is relying on outdated science to support this increase in fluoride exposure.

"In our view [the EPA] has not discharged its legal duty to thoroughly consider the effects of fluoride on infants and children, from all routes of exposure, based on a thorough review of the most recent peer-reviewed science," he said.

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Memorandum of Understanding
Between
The Environmental Protection Agency
and
The Food and Drug Administration

I. Purpose:

This Memorandum of Understanding establishes an agreement between the Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) with regard to the control of direct and indirect additives to and substances in drinking water.

EPA and FDA agree:

A. That contamination of drinking water from the use and application of direct and indirect additives and other substances poses a potential public health problem;

B. That the scope of the additives problem in terms of the health significance of these contaminants in drinking water is not fully known;

C. That the possibility of overlapping jurisdiction between EPA and FDA with respect to control of drinking water additives has been the subject of Congressional as well as public concern;

D. That the authority to control the use and application of direct and indirect additives to and substances in drinking water should be vested in a single regulatory agency to avoid duplicative and inconsistent regulation;

E. That EPA has been mandated by Congress under the Safe Drinking Water Act (SDWA), as amended, to assure that the public is provided with safe drinking water;

F. That EPA has been mandated by Congress under the Toxic Substances Control Act (TSCA) to protect against unreasonable risks to health and the environment from toxic substances by requiring, inter alia, testing and necessary restrictions on the use, manufacture, processing, distribution, and disposal of chemical substances and mixtures;

G. That EPA has been mandated by Congress under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), as amended, to assure, inter alia, that when used properly, pesticides will perform their intended function without causing unreasonable adverse effects on the environment; and,

H. That FDA has been mandated by Congress under the Federal Food, Drug, and Cosmetic Act (FFDCA), as amended, to protect the public from, inter alia, the adulteration of food by food additives and poisonous and deleterious substances. It is the intent of the parties that:

A. EPA will have responsibility for direct and indirect additives to and other substances in drinking water under the SDWA, TSCA, and FIFRA; and,

B. FDA will have responsibility for water, and substances in water, used in food and for food processing and responsibility for bottled drinking water under the FFDCA.

II. Background:

A. FDA Legal Authority

memo-of-understanding-fda-epa-225-79-2001-epa-to-regulate-water-additives
"Food" means articles used for food or drink for man or other animals and components of such articles. (FFDCA Section 201(f)). Under Section 402, inter alia, a food may not contain any added poisonous or deleterious substance that may render it injurious to health, or be prepared, packed or handled under unsanitary conditions. Tolerances may be set, under Section 406, limiting the quantity of any substance which is required for the production of food or cannot be avoided in food. FDA has the authority under Section 409 to issue food additive regulations approving, with or without conditions, or denying the use of a "food additive." That term is defined in Section 201(s) to include any substance the intended use of which results or may reasonably be expected to result, directly or indirectly, in its becoming a component or otherwise affecting the characteristics of any food, if such substance is not generally recognized as safe.

In the past, FDA has considered drinking water to be a food under Section 201(f). However, both parties have determined that the passage of the SDWA in 1974 implicitly repealed FDA's authority under the FFDCA over water used for drinking water purposes. Under the express provisions of Section 410 of the FFDCA, FDA retains authority over bottled drinking water. Furthermore, all water used in food remains a food and subject to the provisions of the FFDCA. Water used for food processing is subject to applicable provisions of FFDCA. Moreover, all substances in water used in food are added substances subject to the provisions of the FFDCA, but no substances added to a public drinking water system before the water enters a food processing establishment will be considered a food additive.

B. EPA Legal Authority

The SDWA grants EPA the authority to control contaminants in drinking water which may have any adverse effect on the public health, through the establishment of maximum contaminant levels (MCLs) or treatment techniques, under Section 1412, which are applicable to owners and operators of public water systems. The expressed intent of the Act was to give EPA exclusive control over the safety of public water supplies. Public water systems may also be required by regulation to conduct monitoring for unregulated contaminants under Section 1445 and to issue public notification of such levels under Section 1414(c).

EPA's direct authority to control additives to drinking water apart from the existence of maximum contaminant levels or treatment techniques is limited to its emergency powers under Section 1431. However, Section 1442(b) of the Act authorizes EPA to "collect and make available information pertaining to research, investigations, and demonstrations with respect to providing a dependably safe supply of drinking water together with appropriate recommendations therewith."

TSCA gives EPA authority to regulate chemical substances, mixtures and under some circumstances, articles containing such substances or mixtures. Section 4 permits EPA to require testing of a chemical substance or mixture based on possible unreasonable risk of injury to health or the environment, or on significant or substantial human or environmental exposure while Section 8 enables EPA to require submission of data showing substantial risk of injury to health or the environment, existing health and safety studies, and other data. For new chemical substances, and significant new uses of existing chemical substances, Section 5 requires manufacturers to provide EPA with pre-manufacturing notice. Under Section 6 the manufacture, processing, distribution, use, and disposal of a chemical substance or mixture determined to be harmful may be restricted or banned. Although Section 3(2)(B) of TSCA excludes from the definition of "chemical substance" food and food additives as defined under FFDCA, the implicit repeal by the SDWA of FDA's authority over drinking water enables EPA to regulate direct and indirect additives to drinking water as chemical substances and mixtures under TSCA.

The FIFRA requires EPA to set restrictions on the use of pesticides to assure that when used properly, they will not cause unreasonable adverse effects on the

memo-of-understanding-fda-epa-225-79-2001-epa-to-regulate-water-additives environment. EPA may require, inter alia labeling which specifies how, when, and where a pesticide may be legally used. In addition, EPA has, under Section 409 of the FFDCA, required FIFRA registrants at times to obtain a food additive tolerance before using a pesticide in or around a drinking water source. Such tolerances establish further restrictions on the use of a pesticide which are enforceable against the water supplier as well as the registrant of the pesticide.

III. Terms of Agreement:

A. EPA's responsibilities are as follows:

1. To establish appropriate regulations, and to take appropriate measures, under the SDWA and/or TSCA, and FIFRA, to control direct additives to drinking water (which encompass any substances purposely added to the water), and indirect additives (which encompass any substance which might leach from paints, coatings or other materials as an incidental result of drinking water contact), and other substances.
2. To establish appropriate regulations under the SDWA to limit the concentrations of pesticides in drinking water; the limitations on concentrations and types of pesticides in water are presently set by EPA through tolerances under Section 409 of the FFDCA.
3. To continue to provide technical assistance in the form of informal advisory opinions on drinking water additives under Section 1442(b) of the SDWA.
4. To conduct and require research and monitoring and the submission of data relative to the problem of direct and indirect additives in drinking water in order to accumulate data concerning the health risks posed by the presence of these contaminants in drinking water.

B. FDA's responsibilities are as follows:

1. To take appropriate regulatory action under the authority of the FFDCA to control bottled drinking water and water, and substances in water, used in food and for food processing.
2. To provide assistance to EPA to facilitate the transition of responsibilities, including:
 - a) To review existing FDA approvals in order to identify their applicability to additives in drinking water.
 - b) To provide a mutually agreed upon level of assistance in conducting literature searches related to toxicological decision making.
 - c) To provide a senior toxicologist to help EPA devise new procedures and protocols to be used in formulating advice on direct and indirect additives to drinking water.

IV. Duration of Agreement:

This Memorandum of Understanding shall continue in effect unless modified by mutual consent of both parties or terminated by either party upon thirty (30) days advance written notice to the other.

This Memorandum of Understanding will become effective on the date of the last signature.

Approved and Accepted
for the Environmental Protection Agency
Signed by: Douglas P. Costle
Administrator
Environmental Protection Agency
Date: June 12, 1979

Approved and Accepted
for the Food and Drug Administration
Signed by: Donald Kennedy
Administrator
Food and Drug Administration

memo-of-understanding-fda-epa-225-79-2001-epa-to-regulate-water-additives
Date: June 22, 1979



July 7, 2000

The Honorable Ken Calvert
Chairman Subcommittee on Energy and the Environment
Committee on Science
U. S. House of Representatives
Suite 2320, Rayburn House Office Building
Washington, DC 20515-6301

Dear Mr. Chairman:

Thank you for your letter of May 8, 2000 to Dr. Joseph Cotruvo wherein you request information from NSF International (NSF) on fluoride containing compounds. We appreciate having received an extension in order to allow NSF staff sufficient time to provide a comprehensive response to your request.

This response is comprised of a general information section entitled *Background on NSF and the Drinking Water Additives Program* and a section that answers the 8 questions in your letter. I have attached additional documents that will also assist in answering your questions.

It is important to note that your questions relate to two separate issues, and departments, within NSF – standards and product certification. First, ANSI/NSF Standard 60 – the American National Standard developed by NSF and a consortium of major stakeholders consisting of the American Water Works Association (AWWA), the AWWA Research Foundation (AWWARF), the Association of State Drinking Water Administrators (ASDWA), and the now inactive Conference of State Health and Environmental Managers (COSHEM) was developed from 1985 to 1987. Second, NSF operates a separate product testing, certification and listing program based on the requirements of the standard.

The health based principles of Standard 60 were originally developed by the NSF Health Advisory Board (HAB) which is a panel of non-NSF health science experts. This group continues its role in an advisory and oversight function to NSF and its Toxicology staff to assure that ANSI/NSF Standards are consistent with current public health principles.

The standard and the certification program are recognized and utilized by AWWA and its member utilities, and adopted in most state regulations. More than 43 states have regulations in place requiring product compliance with ANSI/NSF Standard 60. (See Attachment 14). The program provides a product quality and safety assurance that aims to prevent addition of harmful levels of contaminants from treatment chemicals.

Fluorosilicate products are comprised of a fluoride entity as well as a silicate entity. Based on previously published studies, there is virtually complete dissociation of the fluoride and silicate entities in dilute solutions. As such, the toxicological evaluation of fluorosilicate products is conducted through the evaluation of each entity separately.

ANSI/NSF Standard 60 requires, when available, that the U.S. EPA regulated Maximum Contaminant Level (MCL) be used to determine the acceptable level for a contaminant. The MCL for fluoride is 4 mg/L of drinking water. As such, NSF has not independently developed toxicology data to support this level of human exposure. The Maximum Allowable Level (MAL) for fluoride ion in drinking water from NSF Certified treatment chemicals is 1.2 mg/L, or less than one-third the EPA's MCL. The product Maximum Use Level (MUL) certified by NSF ranges from 4 - 6.6 mg/L.

There is no EPA MCL for silicate in drinking water. When an MCL does not exist for a contaminant, ANSI/NSF Standard 60 provides criteria to conduct a toxicological risk assessment of the contaminant and the development of a Maximum Drinking Water Level (MDWL). NSF has established a Maximum Drinking Water Level of silicate at 16 mg/L. A fluorosilicate product MUL of 4-6.6 mg/L results in silicate drinking water levels substantially below the 16 mg/L MAL established by NSF for silicates. Attachment 15 outlines the derivation of the NSF MAL for silicates.

In general, NSF Certified fluoridation products have been tested and found to comply with the requirements of ANSI/NSF Standard 60 for 12 additional inorganic chemicals. Additional testing of these products for radionuclides has resulted in no measurements above the detection limits. The specific answers below provide additional detail.

If there is any more information that you need, please do not hesitate to contact me.

Sincerely,



Stan Hazan
General Manager
Drinking Water Additives Certification Program
734-769-5105
hazan@nsf.org

cc: Dr. Joe Cotruvo, NSF
Dr. Lori Bestervelt, NSF

List of Attachments

Attachment	Description
1	FR Notice 5/17/84 - Disposition of the Federal DWA Advisory Program
2	FR Notice 7/7/88 - Termination of the Federal DWA Program, Notice
3	ANSI/NSF Standard 60 - DW Treatment Chemicals- Health Effects
4	ANSI/NSF Standard 61 - DW System Components- Health Effects
5	NSF Standards Development and Maintenance Policies
6	Standards Update - Flowchart of the Standards Development Process
7	1987 NSF DWA Joint Committee Membership List
8	1987 NSF Council of Public Health Consultants List
9	NSF Certification Policies for DW Treatment Chemicals - Standard 60
10	Toxicology Data Review Submission Form - Part A
11	Toxicology Data Review Submission Form - Part B
12	NSF DWA Listings Book
13	NSF DWA Certification Process - 7 Steps
14	ASDWA State Survey of Adoption of ANSI/NSF Standards 60 and 61
15	NSF MAL Derivation for Silicates in Drinking Water

Background on NSF and the Drinking Water Additives Program.

NSF International was established in 1944, as an independent, not-for-profit, third party organization dedicated to the protection of public health and safety. NSF has more than 300 employees consisting of engineers, chemists and toxicologists who develop U.S. national standards and provide independent product testing and certification services for products that impact food, air, water and the environment. NSF is a World Health Organization (WHO) Collaborating Center on Drinking Water Safety and Treatment, as well as for Food Safety.

★ NSF involvement in the evaluation of drinking water chemicals, including fluoride-based chemicals, began in 1985, when the U.S. EPA granted an NSF-led consortium of stakeholders the responsibility to develop consensus, health-based, quality specifications for drinking water treatment chemicals and drinking water system components (Attachment 1). EPA also requested development of a product testing and certification program that would allow for independent product evaluations for use by states, cities, and water utilities, as a basis for product acceptance and use.

The original goal of the standard and certification program was to develop a preventative mechanism for selecting treatment chemicals that would not contribute harmful levels of contaminants to drinking water. The standards and the certification program were designed to be dynamic, to change as regulations change, and to constantly be tied to the requirements of the Safe Drinking Water Act and its drinking water quality regulations. In 1988, EPA terminated its informal chemical additives advisory program upon completion of the NSF standards and successful launch of the NSF product certification program (Attachment 2). We believe that the NSF standards and certification program have succeeded in achieving the goals of the original mandate. ★

The NSF Certification program consists of seven steps for initial product certification, and 4 steps on an annual basis. (See Attachment 13).

Today, NSF provides testing and certification services for thousands of products from more than 30 countries. NSF publishes its listings on its web site at www.nsf.org as well as in hardcopy (Attachment 12). In addition, attached is a copy of the NSF Certification Policies for Drinking Water Treatment Chemicals (Attachment 9). This document outlines the rules that govern the product certification program, over and above the requirements of the standard.

This section provides responses to the 8 questions in your letter.

Question 1. Please provide the identification and affiliation of each member of the committee or committees contributing to the policies established for each of the fluorine-bearing additives destined for the public water supplies, both current committee members and those responsible for establishing product standards for fluoride.

In response to an identified need for health-based standards dealing with drinking water contact products, a consortium led by the National Sanitation Foundation (now NSF) worked to develop voluntary third-party consensus standards for all direct and indirect drinking water additives. Other consortium members were the American Water Works Association (AWWA), the American Water Works Association Research Foundation (AWWARF), the Association of State Drinking Water Administrators (ASDWA) and the Conference of State Health and Environmental Managers (COSHEM, now inactive).

ANSI/NSF 60 Drinking water treatment chemicals – Health effects was initially adopted in December 1987, and was last revised in May 2000. It establishes minimum human health effects requirements for the chemicals that are added directly to drinking water for its treatment or other purposes. The standard was developed using a consensus standards development process with representation of the major stakeholder interests, including product manufacturers, product users such as consultants and water utilities, and representatives from the regulatory/public health sectors. As an American National Standard, each revision to ANSI/NSF 60 also undergoes a public comment review. This public comment process allows for any interested party to obtain a copy of the proposed revision and to submit comments or objections to NSF. All comments received are handled in accordance with the due-process requirements set forth in the ANSI procedures and NSF policies.

Each edition of ANSI/NSF 60 contains a list of the committee members who oversee the development and review of that edition of the standard. These committees consist of the NSF Joint Committee for Drinking Water Additives, the balanced group of approximately 36 representatives from the user, regulatory and manufacturing sectors, and the NSF Council of Public Health Consultants, which is a group of approximately 45 independent, public health experts from government, academia and the environmental health community. The current version of ANSI/NSF 60 (2000) is enclosed for your review (Attachment 3), as well as a list of the membership of these committees when the Standard was first adopted in 1987 (Attachments 7 and 8). Copies of the *NSF Standards Development and Maintenance Policies* (Attachment 5) and "Standards Update" (Attachment 6) are also enclosed to provide further detail on the standards development process.

Question 2. Under General Requirements 3.2.1, formulation submission and review, ANSI/NSF 60 -1999, are manufacturers of hydrofluosilicic acid and silicofluorides required to "submit for each product, when available, a list of published and unpublished toxicological studies relevant to the treatment chemical and the chemicals and impurities present in the treatment chemical?"

The standard requires that the manufacturer of a product submitted for certification provide toxicological information, if available. NSF requires that manufacturers seeking certification to the standard submit this information as part of their formulation or ingredient supplier submission. ✓

Has your document, General Requirements 3.2.1, Formulation submission and review, ANSI/NSF 60 - 1999, been peer reviewed for accuracy? If so, please provide the names, affiliations and contact information for the peer reviewers.

The document (ANSI/NSF Standard 60) has been peer reviewed for accuracy. Joint Committee and CPHC members and contact information are contained in Attachments 3, 7, and 8.

Please provide:

All lists complying with the above requirement submitted by manufacturers of hydrofluosilicic acid and silicofluorides.

NSF has based its certification on the product use not exceeding the EPA's MCL for fluoride. Separately, NSF has developed an MAL for silicates of 16 mg/L that supports the silicate portion of the products in question. In addition, potential contaminants are also limited by the standard. The supporting rationale for the silicate MAL is enclosed in Attachment 15.

The complete record of all tests of each fluorine-bearing additive using ion chromatography, atomic absorption spectroscopy, and scintillation counting.

NSF toxicology review and testing of fluorosilicate compounds looks for potential trace contaminants such as heavy metals and radionuclides. The formulation review step examines not only the product formulation, but also considers potential contaminants from the ingredients, processing aids, and any other factors impacting contaminants in the finished drinking water. Contaminants in the finished drinking water are not permitted to exceed one-tenth of the EPA's regulated MCL (Maximum Contaminant Level) when the product is added to drinking water at its Maximum Use Level, unless it can be documented that a limited number of sources of the contaminant occur in drinking water.

NSF has reviewed its files and has compiled a summary of our findings (Table 1) in lieu of complete test reports. Individual test reports, as well as formulation information are protected by nondisclosure agreements with certification clients.

NSF searched its files to determine the level of contaminants found in these fluoridation products, when the product is dosed to water at the Maximum Use Level (MUL). The exact number of laboratory tests performed is not readily available

because we maintain records only on those tests where a contaminant was detected. The results in Table 1 include initial product tests as well as annual product monitoring tests. In total, these products have been tested more than 100 times in our laboratories. Table 1 indicates that metals contamination of drinking water as a result of fluoride chemical use is not an issue. There has not been a single fluoride product tested with a metal concentration in excess of its corresponding MAL.

Silica and silicates, which make up a portion of the fluoridation chemicals mentioned above, are addressed by the certification of sodium silicates to a level of 16 mg/L under ANSI/NSF Standard 60. (See Attachment 15).

Beginning in early 1998, NSF went beyond Standard 60 requirements and voluntarily began testing fluoridation chemicals for the presence of radionuclides (alpha and beta emitters) utilizing EPA Test Method 900.0, as specified in Annex B of ANSUNSF Standard 60. To date, we have not found any sample with a positive (detected) result, with detection limits of 4 pCi/liter and 3 pCi/liter for gross alpha and gross beta, respectively.

Table 1

	Number of Fluoride Samples with Positive Test Results	Average Contaminant Concentration in Samples with Positive Test Results* (ppb)	Maximum Contaminant Concentration in Samples with Positive Test Results (ppb)	ANSI/NSF Standard 60 Maximum Allowable Level (MAL) (ppb)	US EPA Maximum Contaminant Level (MCL) (ppb)
Antimony	0	NA	NA	0.6	6
Arsenic	39	0.43	1.66	2.5**	50
Barium	1	0.19	0.17	200	2000
Beryllium	5	0.21	0.3	0.4	4
Cadmium	3	0.06	0.1	0.5	5
Chromium	3	0.14	0.2	10	100
Copper	8	0.49	0.55	130	1300
Lead	7	0.4	1.1	1.5	15
Mercury	5	0.013	0.015	0.2	2
Nickel	0	NA	NA	NA	NA
Selenium	1	0.60	0.6	5	50
Thallium	6	0.03	0.05	0.2	2
Radionuclides	0	NA	NA	-	-

**Only those samples where a contaminant was detected contribute to the average. The average contaminant concentration for all samples tested is significantly lower, and is affected by detection limits and number of detections.*

*** ANSI/NSF Std 60 utilizes Canadian MACs and EPA MCLs in determination of MALs.*

A true and complete copy of all tests that identify the full composition of each fluorine-bearing additive, including all attendant organic substances, radionuclides and other chemicals.

Compositional analyses are not required by the NSF standard. The verification of composition is performed during the annual unannounced plant inspection by NSF auditors who verify sources and ratios of labeled ingredients. Separately, there are industry standards from AWWA (American Water Works Association) (ANSI/AWWA B702-99 for Sodium Fluorosilicate and ANSI/AWWA B703a-97 for Fluosilicic Acid) that provide for compositional requirements.

Copies of any and all tests or studies of each of the fluorine-bearing additives that consider or indicate degree of dissociation.

The standard requires testing for contaminants that are likely to be present in the product. A study by N.T. Crosby, published in 1969 in the Journal of Applied Chemistry (Volume 19), establishes dissociation of fluorosilicates at 99% for 1ppm fluoride concentrations in drinking water.

Copies of any and all studies that have been performed on laboratory animals using hydrofluosilicic acid or silicofluorides.

NSF does not perform animal testing, although these may be required under Standard 60 if hazard/risk based action levels are exceeded. NSF toxicologists may review animal studies during the toxicology evaluation step of the product certification process.

Copies of any risk assessment documents in NSF International files that pertain to fluorine-bearing pesticides, such as cryolite.

Fluorine-containing pesticides such as cryolite are not required analyses under the standard, unless it is determined to be part of the formulation, or a potential contaminant. NSF would test for this or any other contaminants if indicated during the formulation review step.

Question 3. Have any studies on hydrofluosilicic acid or silicofluorides been submitted to NSF under claimed Confidential Business Information protection?

There have not been any studies on hydrofluosilicic acid or silicofluorides submitted to NSF under claimed Confidential Business Information protection.

Question 4. What are the Maximum Contaminant Levels, or any other regulatory standards, established for the following contaminants (either singularly, in combination with another substance, or in the elements' various forms) or any other contaminants reported as present in the fluorine-bearing substances hydrofluosilicic acid and other silicofluorides used in fluoridation programs?

Maximum Contaminant Levels (MCLs) can be found in Annex E of the enclosed copy of ANSI/NSF 60. Annex E of Standard 60 lists the federally regulated MCLs. Of the contaminants listed in your letter, MCLs exist for arsenic, barium, beryllium, cadmium, chromium, fluoride, lead, mercury, selenium, and dioxin (as 2,3,7,8-TCDD). Federal regulatory standards have not been established for the remaining contaminants listed in your letter.

Question 5. What tests are performed to identify the full and exact consistency of the fluorine-bearing product and determine the concentrations of each of the contaminants or combination of contaminants in a sample? Upon what occasion or frequency are these tests performed? Are Certificates of Analysis provided with each shipment of such products from the manufacturer?

NSF tests certified products at least annually for prospective contaminants (See response to Question 2). An NSF Certified company may produce many shipments during the course of the year, but the company is contractually bound to not change the formulation ratios, ingredients or add unauthorized sources of supply. Certificates of Analyses are typically provided by the vendor to the utility on a per shipment basis. There are industry standards from AWWA (American Water Works Association) (ANSI/AWWA B702-99 for Sodium Fluorosilicate and ANSI/AWWA B703a-97 for Fluosilicic Acid) that provide for affidavits and Certificates of Analyses.

Question 6. What is the purpose of establishing a maximum allowable level (MAL) for additives, restricting the contribution to drinking water of any one product to 10% of the Maximum Contaminant Level (MCL)?

The purpose of establishing a maximum allowable level (MAL) for individual drinking water additives products at 10% of the MCL is to recognize that contaminants may enter drinking water from other points throughout the system, including the source water, during the treatment and distribution process, and either through direct addition or surface contact. Limiting individual products to a contribution of 10% of the MCL for a given contaminant provides an extra margin of safety so that it is unlikely that the summation of the contributions from all potential sources will exceed the MCL at the tap.

Question 7. Under what circumstances or authority is an additive certified when the MAL of 10% of the established MCL is exceeded?

An MAL of greater than 10% of the MCL can be established by the certification body in limited cases if it can be reasonably documented that there are no other significant sources of the same contaminant, that together, would result in the finished drinking water contaminant concentration exceeding the MCL. Fluoride has an MAL of 1.2 mg / liter, which is 30% of the MCL. This is justified on the basis of the limited number of other potential sources of fluoride ion to drinking water. For example, water that naturally contains sufficient fluoride is not additionally fluoridated, and fluoride is seldom present in other additives.

Question 8. What tests and how often are they performed by NSF International to determine the exact consistency and concentrations of all contaminants in hydrofluosilicic acid, silicofluorides and sodium fluoride products? What is the ratio of NSF International tests to shipments by manufacturers of the additives? Are NSF International test results compared with Certificates of Analyses as a quality assurance measure?

As indicated in question 2, the testing required by the standard is for regulated metals. NSF additionally performs radionuclides analysis. Contaminant testing is performed initially upon application, and at least annually thereafter. Samples are collected during unannounced inspections by NSF auditors.

As mentioned previously, NSF tests products at least once per year. A contract signed by the NSF Certified manufacturer precludes production or process changes without written consent from NSF.

NSF test results are not routinely compared to Certificate of Analyses results. Certificates of Analyses often report on parameters not required under ANSVNSF Standard 60. For example, the AWWA standards mentioned previously require testing for fluoride content, moisture, impurities, etc. The AWWA standards also incorporate the option of additional purchaser specifications.

Please provide the committee with copies of any NSF International publications, studies, and reports relating to fluoride.

As mentioned earlier, NSF relies on the U.S. EPA MCL and its supporting documentation, as specified in the standard. See attachments listed in the cover letter.

Fluorine-containing pesticides and pharmaceuticals also contribute to total fluorine exposures and are considered separately. Fluoride in food and drinking water usually is considered in terms of total fluorine content, assumed to be present entirely as fluoride ion (F^-). Information on exposures to fluorosilicates and aluminofluorides is also included.

SOURCES OF FLUORIDE EXPOSURE

Drinking Water

General Population

The major dietary source of fluoride for most people in the United States is fluoridated municipal (community) drinking water, including water consumed directly, food and beverages prepared at home or in restaurants from municipal drinking water, and commercial beverages and processed foods originating from fluoridated municipalities. On a mean per capita basis, community (public or municipal) water constitutes 75% of the total water ingested in the United States; bottled water constitutes 13%, and other sources (e.g., wells and cisterns) constitute 10% (EPA 2000a). Municipal water sources that are not considered "fluoridated" could contain low concentrations of naturally occurring fluoride, as could bottled water and private wells, depending on the sources.

An estimated 162 million people in the United States (65.8% of the population served by public water systems) received "optimally fluoridated"¹ water in 2000 (CDC 2002a). This represents an increase from 144 million (62.1%) in 1992. The total number of people served by public water systems in the United States is estimated to be 246 million; an estimated 35 million people obtain water from other sources such as private wells (CDC 2002a,b). The U.S. Environmental Protection Agency (EPA) limits the fluoride that can be present in public drinking-water supplies to 4 mg/L (maximum contaminant level, or MCL) to protect against crippling skeletal fluorosis, with a secondary maximum contaminant level (SMCL) of 2 mg/L to protect against objectionable dental fluorosis (40CFR 141.62(b)[2001], 40CFR 143.3[2001]).

Of the 144 million people with fluoridated public water supplies in 1992, approximately 10 million (7%) received naturally fluoridated water, the rest had artificially fluoridated water (CDC 2002c). Of the population with artificially fluoridated water in 1992, more than two-thirds had a water fluoride concentration of 1.0 mg/L, with almost one-quarter having lower concentrations and about 5% having concentrations up to 1.2 mg/L (CDC 1993; see Appendix B).

Of the approximately 10 million people with naturally fluoridated public water supplies in 1992, approximately 67% had fluoride concentrations ≤ 1.2 mg/L (CDC 1993; see Appendix B). Approximately 14% had fluoride concentrations between 1.3 and 1.9 mg/L and another 14% had between 2.0 and 3.9 mg/L; 2% (just over 200,000 persons) had natural fluoride

¹The term optimally fluoridated water means a fluoride level of 0.7-1.2 mg/L; water fluoride levels are based on the average maximum daily air temperature of the area (see Appendix B).



NSF Fact Sheet on Fluoridation Chemicals

Introduction

This fact sheet provides information on the fluoride containing water treatment additives that NSF has tested and certified to NSF/ANSI Standard 60: Drinking Water Chemicals - Health Effects. According to the latest Association of State Drinking Water Administrators Survey on State Adoption of NSF/ANSI Standards 60 and 61, 45 states require that chemicals used in treating potable water must meet Standard 60 requirements. If you have questions on your state's requirements, or how the NSF/ANSI Standard 60 certified products are used in your state, you should contact your state's Drinking Water Administrator.

Water fluoridation is the practice of adjusting the fluoride content of drinking water. Fluoride is added to water for the public health benefit of preventing and reducing tooth decay and improving the health of the community. The U.S. Centers for Disease Control and Prevention is a reliable source of information on this important public health intervention. For more information please visit www.cdc.gov/fluoridation/.

NSF certifies three basic products in the fluoridation category:

1. Fluorosilicic Acid (aka Fluosilicic Acid or Hydrofluosilicic Acid).
2. Sodium Fluorosilicate (aka Sodium Silicofluoride).
3. Sodium Fluoride.

NSF Standard 60

Products used for drinking water treatment are evaluated to the criteria specified in NSF/ANSI Standard 60. This standard was developed by an NSF-led consortium, including the American Water Works Association (AWWA), the American Water Works Association Research Foundation (AWWARF), the Association of State Drinking Water Administrators (ASDWA), and the Conference of State Health and Environmental Managers (COSHEM). This group developed NSF/ANSI Standard 60, at the request of the US EPA Office of Water, in 1988. The NSF Joint Committee on Drinking Water Additives continues to review and maintain the standard annually. This committee consists of representatives from the original stakeholder groups as well as other regulatory, water utility and product manufacturer representatives.

Standard 60 was developed to establish minimum requirements for the control of potential adverse human health effects from products added directly to water during its treatment, storage and distribution. The standard requires a full formulation disclosure of each chemical ingredient in a product. It also requires a toxicology review to determine that the product is safe at its maximum use level and to evaluate potential contaminants in the product. The standard requires testing of the treatment chemical products, typically by dosing these in water at 10 times the maximum use level, so that trace levels of contaminants can be detected. A toxicology evaluation of test results is required to determine if any contaminant concentrations have the potential to cause adverse human health effects. The standard sets criteria for the establishment of single product allowable concentrations (SPAC) of each respective contaminant. For contaminants regulated by the U.S. EPA, this SPAC has a default level not to exceed ten-percent of the regulatory level to provide protection for the consumer in the unlikely event of multiple sources of the contaminant, unless a lower or higher number of sources can be specifically identified.

NSF Certification

NSF also developed a testing and certification program for these products, so that individual U.S. states and waterworks facilities would have a mechanism to determine which products were appropriate for use. The certification program requires annual unannounced inspections of production and distribution facilities to ensure that the products are properly formulated, packaged, and transported with safe guards against potential contamination. NSF also requires annual testing and toxicological evaluation of each NSF Certified product. NSF Certified products have the NSF Mark, the maximum use level, lot number or date code and production location on the product packaging or documentation shipped with the product.

The use of this standard and the associated certification program have yielded benefits in ensuring that drinking water additives meet the health objectives that provide the basis for public health protection. NSF maintains listings of companies that manufacture and distribute treatment products at www.nsf.org. These listings are updated daily and list the products at their allowable maximum use levels. In recognition of the important safeguards that NSF Standard 60 provides to public drinking water supplies, 45 U.S. States and 10 Canadian Provinces and Territories require drinking water treatment chemicals to comply with the requirements of the standard.

Treatment products that are used for fluoridation are addressed in Section 7 of NSF/ANSI Standard 60. The products are allowed to be used up to concentrations that result in a maximum use level of 1.2 mg/L fluoride ion in water. The NSF standard requires that the treatment products added to drinking water, as well as any impurities in the products, are supported by toxicological evaluation. The following text explains the rationale for the allowable levels established in the standard for 1) fluoride, 2) silicate, and 3) other potential contaminants that may be associated with fluoridation chemicals.

Fluoride

NSF/ANSI Standard 60 requires, when available, that the US EPA regulated maximum contaminant level (MCL) be used to determine the acceptable level for a contaminant. The EPA MCL for fluoride ion in water is 4 mg/L. The NSF Standard 60 single product allowable concentration (SPAC) for fluoride ion in drinking water from NSF Certified treatment products is 1.2 mg/L, or less than one-third of the EPA's MCL. Based on this the allowable maximum use level (MUL) for the NSF Certified fluoridation products are:

1. Fluorosilicic Acid: 6 mg/L.
2. Sodium Fluorosilicate: 2 mg/L.
3. Sodium Fluoride: 2.3 mg/L.

Silicate

There is no EPA MCL for silicate in drinking water. When an MCL does not exist for a contaminant, NSF/ANSI Standard 60 provides criteria to conduct a toxicological risk assessment of the contaminant and the development of a SPAC. NSF has established a SPAC for silicate at 16 mg/L. A fluorosilicate product, applied at its maximum use level, results in silicate drinking water levels that are substantially below the 16 mg/L SPAC established by NSF. For example, a sodium fluorosilicate product dosed at a concentration into drinking water that would provide the maximum concentration of fluoride allowed (1.2mg/L) would only contribute 0.8 mg/L of silicate – or 5 percent of the SPAC allowed by NSF 60.

Potential Contaminants

The NSF toxicology review for a chemical product considers all chemical ingredients in the product as well as the manufacturing process, processing aids, and other factors that have an impact on the contaminants present in the finished drinking water. This formulation review identifies all the contaminants that need to be analyzed in testing the product. For example, fluosilicic acid is produced by adding sulfuric acid to phosphate ore. This is typically done during the production of phosphate additives for agricultural fertilizers. The manufacturing process is documented by an NSF inspector at an initial audit of the manufacturing site and during each annual unannounced inspection of the facility. The manufacturing process, ingredients, and potential contaminants are reviewed annually by NSF toxicologists, and the product is tested for any potential contaminants. A minimum test battery for all fluoridation products includes metals of toxicological concern and radionuclides.

Many drinking water treatment additives, including fluoridation products, are transported in bulk via tanker trucks to terminals where they are transferred to rail cars, shipped to distant locations or transferred into tanker trucks, and then delivered to the water treatment plants. These tanker trucks, transfer terminals and rail cars are potential sources of contamination. Therefore, NSF also inspects, samples, tests, and certifies products at rail transfer and storage depots. It is always important to verify that the location of the product distributor (the company that delivers the product to the water utility) matches that in the official NSF Listing for the product (available at www.nsf.org).

NSF has compiled data on the level of contaminants found in all fluoridation products that have applied for, or have been listed by, NSF. The statistical results in Table 1 (attached) include the test results for these products, as well as the annual monitoring tests from the period 2000 to 2006. This includes 245 separate samples analyzed during this time period. The concentrations reported represent contaminant levels that would be expected when the product is dosed into water at the Maximum Use Level (MUL). Lower product doses would produce proportionately lower contaminant concentrations (e.g. a 0.6 mg/L fluoride dose would produce one half the contaminant concentrations listed in Table 1.)

Table 1 documents that there is no contamination of drinking water from the fluoridation products NSF has tested and certified. NSF issued previous summaries of contaminant levels in fluoridation products for earlier reporting periods in 1999 and 2003. While some contaminant levels in those earlier periods were slightly higher than the current data for certain contaminants, there has not been a single fluoride product tested since the initiation of the program in 1988 with a contaminant concentration in excess of its corresponding SPAC. The documented reduction of impurities for this most current time period is due, at least in part, to the effectiveness of NSF/ANSI Standard 60 and the NSF certification program for drinking water treatment additives, and demonstrates the effectiveness of the program. The reduction in impurities is further attested to by an article in the Journal of the American Water Works Association entitled, "Trace Contaminants in Water Treatment Chemicals."¹

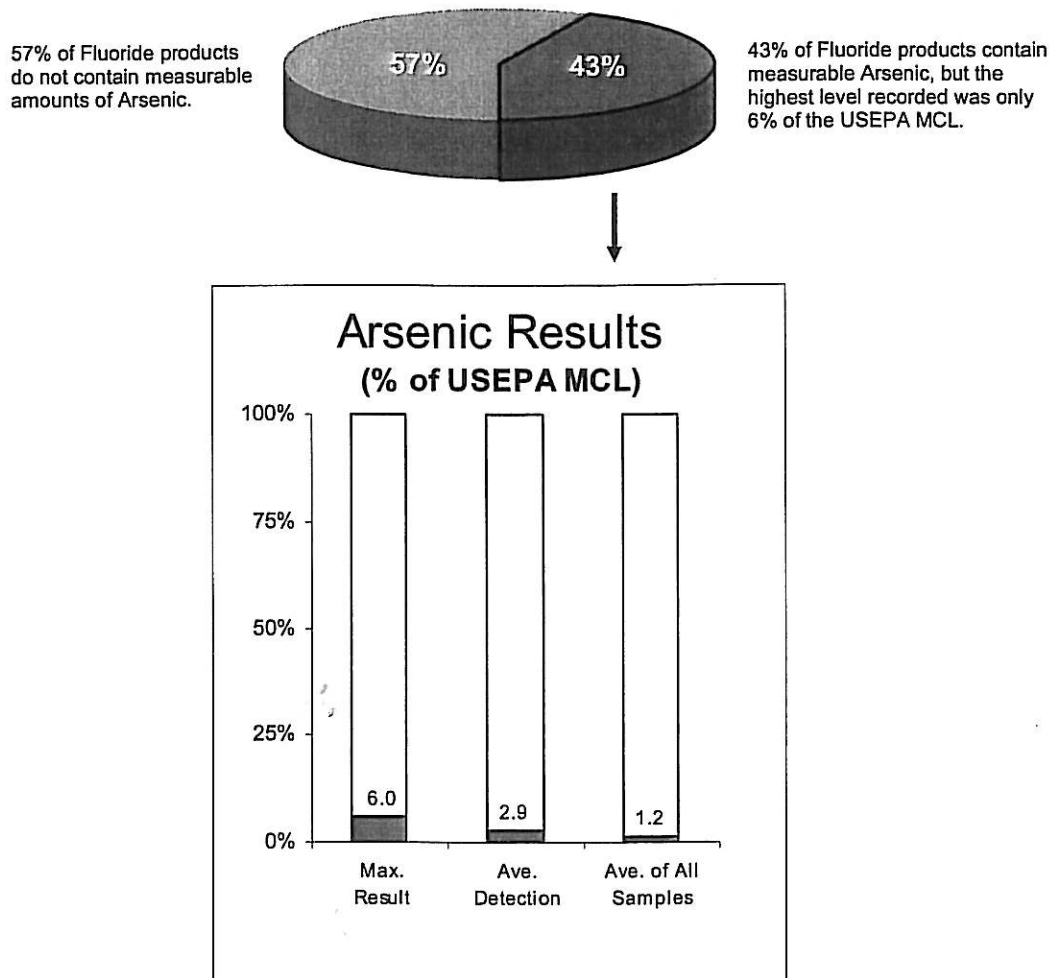
Arsenic

The results in Table 1 indicate that the most common contaminant detected in these products is arsenic, but it is detected in only 43% of the product samples. This means that levels of arsenic

¹ Brown, R., et al., "Trace Contaminants in Water Treatment Chemicals: Sources and Fate." Journal of the American Water Works Association 2004: 96:12:111.

in 57% of the samples were non-detectable, even though products are tested at 10 times their maximum use level. All detections were at levels below the Single Product Allowable Concentration, if the product is added to drinking water at (or below) its maximum use level. The SPAC, as defined in NSF/ANSI Standard 60, is one tenth of the US EPA's MCL. The current MCL for arsenic is 10 ppb, the highest detection of arsenic from a fluoridation chemical was 0.6 ppb (shown on Table 1), and the average concentration was 0.12 ppb. Even the highest concentration of 0.6 ppb was only detected because the standard requires testing the chemical at 10 times its maximum use level to detect these trace levels of contaminants. Had the dose of fluoridation additives been tested in water at the maximum use level, instead of at 10 times their maximum use levels, the arsenic concentration measured would have been below the 1 ppb reporting limit for arsenic for 100 percent of the samples measured.

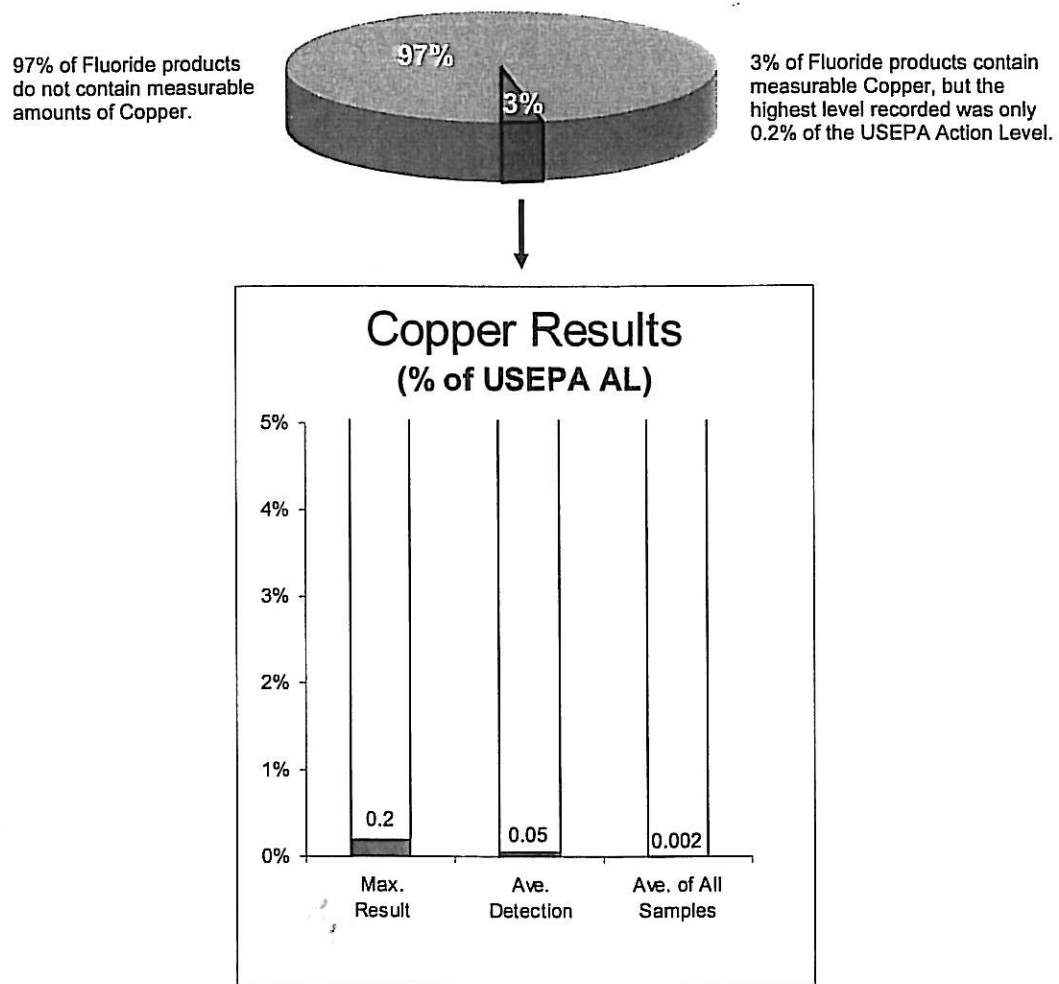
Figure A



Copper

The second most common contaminant found, and on a much less frequent basis, is copper, and 97% of all samples tested had no detectable levels of copper. The average concentration of copper has been 0.02 ppb with 2.6 ppb being the highest concentration detected. This is well below the 130 ppb SPAC requirement of NSF 60.

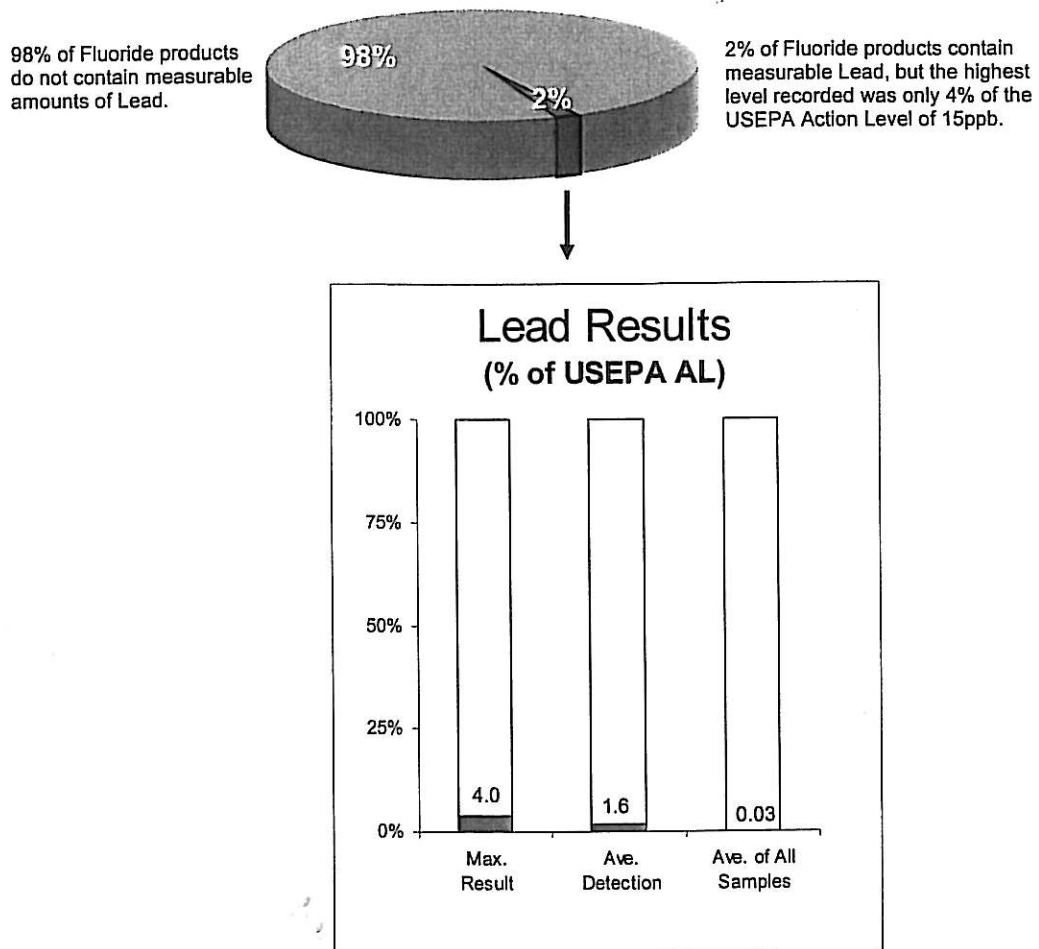
Figure B



Lead

The third most common contaminant found is lead. It occurs on a much less frequent basis, and 98% of all samples tested had no detectable levels of lead. The average concentration of lead has been 0.005 ppb with 0.6 ppb being the highest concentration detected. This is well below the 1.5 ppb SPAC requirement of NSF 60.

Figure C



Radionuclides

Fluoridation products are also tested for radionuclides. All samples tested have not had any detectable levels of alpha or beta radiation.

Summary

In summary, the majority of fluoridation products as a class, based on NSF test results, do not add measurable amounts of arsenic, lead, other heavy metals, or radionuclide contamination to drinking water.

Additional information on fluoridation of drinking water can be found on the following web sites:

American Water Works Association (AWWA) Fluoridation Chemical Standards

<http://www.awwa.org/Bookstore/producttopicsresults.cfm?MetaDataID=121&navItemNumber=5093>

American Water Works Association (AWWA) position

<http://www.awwa.org/Advocacy/pressroom/fluoride.cfm>

American Dental Association (ADA) <http://www.ada.org/public/topics/fluoride/index.asp>

U.S. Centers for Disease Control and Prevention (CDC) <http://www.cdc.gov/fluoridation>

Table 1

	Percentage of Samples with Detectable Levels	Mean Contaminant Concentration in all samples (ppb)	Mean Contaminant Concentration in detectable samples (ppb)	Maximum Contaminant Concentration in detectable samples (ppb)	NSF/ANSI Standard 60 Single Product Allowable Concentration	US EPA Maximum Contaminant or Action Level
Antimony	0%	ND	ND	ND	0.6	6
Arsenic	43%	0.12	0.29	0.6 ✓	1	10
Barium	<1%	0.001	0.3	0.3	200	2000
Beryllium	0%	ND	ND	ND	0.4	4
Cadmium	1%	0.001	0.08	0.12	0.5	5
Chromium	<1%	0.001	0.15	0.2	10	100
Copper	3%	0.02	0.68	2.6	130	1300
Lead	2%	0.005	0.24	0.6 ✓	1.5	15
Mercury	<1%	0.0002	0.04	0.04	0.2	2
Radionuclides – alpha pCi/L	0%	ND	ND	ND	1.5	15
Radionuclides – beta mrem/yr	0%	ND	ND	ND	0.4	4
Selenium	<1%	0.016	1.95	3.2	5	50
Thallium	<1%	0.0003	0.04	0.06	0.2	2

Abbreviations used in this Fact Sheet

ANSI – American National Standards Institute

AWWA – American Water Works Association

AWWARF – American Water Works Association Research Foundation

ASDWA – Association of State Drinking Water Administrators

COSHEM – Conference of State Health and Environmental Managers

EPA – U.S. Environmental Protection Agency

MCL – maximum contaminant level

mrem/yr – millirems per year – measurement of radiation exposure dose

MUL – Maximum use level

NSF – NSF International (formerly the National Sanitation Foundation)

ppb – parts per billion

PCi/L – pico curies per liter – concentration of radioactivity

SPAC – Single Product Allowable Concentration

§ 141.51

- (10) 1,2-Dichloropropane
 (11) Epichlorohydrin
 (12) Ethylene dibromide
 (13) Heptachlor
 (14) Heptachlor epoxide
 (15) Pentachlorophenol
 (16) Polychlorinated biphenyls (PCBs)
 (17) Tetrachloroethylene
 (18) Toxaphene
 (19) Benzo[a]pyrene
 (20) Dichloromethane (methylene chloride)
 (21) Di(2-ethylhexyl)phthalate
 (22) Hexachlorobenzene
 (23) 2,3,7,8-TCDD (Dioxin)
 (b) MCLGs for the following contaminants are as indicated:

Contaminant	MCLG in mg/l
(1) 1,1-Dichloroethylene	0.007
(2) 1,1,1-Trichloroethane	0.20
(3) para-Dichlorobenzene	0.075
(4) Aldicarb	0.001
(5) Aldicarb sulfide	0.001
(6) Aldicarb sulfone	0.001
(7) Alrazine	0.003
(8) Carbofuran	0.04
(9) o-Dichlorobenzene	0.6
(10) cis-1,2-Dichloroethylene	0.07
(11) trans-1,2-Dichloroethylene	0.1
(12) 2,4-D	0.07
(13) Ethylbenzene	0.7
(14) Lindane	0.0002
(15) Methoxychlor	0.04
(16) Monochlorobenzene	0.1
(17) Styrene	0.1
(18) Toluene	1
(19) 2,4,5-TP	0.05
(20) Xylenes (total)	10
(21) Dalapon	0.2
(22) Di(2-ethylhexyl)adipate	.4
(23) Dinoseb	.007
(24) Diquat	.02
(25) Endosulf	.1
(26) Endrin	.002
(27) Glyphosate	.7
(28) Hexachlorocyclopentadiene	.05
(29) Oxamyl (Vydate)	.2
(30) Picloram	.5
(31) Simazine	.004
(32) 1,2,4-Trichlorobenzene	.07
(33) 1,1,2-Trichloroethane	.003

[50 FR 46901, Nov. 13, 1985, as amended at 52 FR 20674, June 2, 1987; 52 FR 25716, July 8, 1987; 56 FR 3592, Jan. 30, 1991; 56 FR 30280, July 1, 1991; 57 FR 31846, July 17, 1992]

§ 141.51 Maximum contaminant level goals for inorganic contaminants.

- (a) [Reserved]
 (b) MCLGs for the following contaminants are as indicated:

40 CFR Ch. I (7-1-03 Edition)

Contaminant	MCLG (mg/l)
Antimony	0.006
Arsenic	zero ¹
Asbestos	7 Million fibers/liter (longer than 10 µm).
Barium	2
Beryllium	.004
Cadmium	0.005
Chromium	0.1
Copper	1.3
Cyanide (as free Cyanide)	.2
Fluoride	4.0
Lead	zero
Mercury	0.002
Nitrate	10 (as Nitrogen).
Nitrite	1 (as Nitrogen).
Total Nitrate+Nitrite	10 (as Nitrogen).
Selenium	0.05
Thallium	.0005

¹ This value for arsenic is effective January 23, 2006. Until then, there is no MCLG.

[50 FR 47155, Nov. 14, 1985, as amended at 52 FR 20674, June 2, 1987; 56 FR 3593, Jan. 30, 1991; 56 FR 26548, June 7, 1991; 56 FR 30280, July 1, 1991; 57 FR 31846, July 17, 1992; 60 FR 33932, June 29, 1995; 66 FR 7063, Jan. 22, 2001]

§ 141.52 Maximum contaminant level goals for microbiological contaminants.

MCLGs for the following contaminants are as indicated:

Contaminant	MCLG
(1) <i>Giardia lamblia</i>	zero
(2) Viruses	zero
(3) <i>Legionella</i>	zero
(4) Total coliforms (including fecal coliforms and <i>Escherichia coli</i>).	zero.
(5) <i>Cryptosporidium</i>	zero.

[54 FR 27527, 27566, June 29, 1989; 55 FR 25064, June 19, 1990; 63 FR 69515, Dec. 16, 1998]

§ 141.53 Maximum contaminant level goals for disinfection byproducts.

MCLGs for the following disinfection byproducts are as indicated:

Disinfection byproduct	MCLG (mg/L)
Bromodichloromethane	Zero
Bromoform	Zero
Bromate	Zero
Dichloroacetic acid	Zero
Trichloroacetic acid	0.3
Chlorite	0.8
Dibromochloromethane	0.06

[63 FR 69465, Dec. 16, 1998, as amended at 65 FR 34405, May 30, 2000]

B-35

Arsenic

From Wikipedia, the free encyclopedia

Arsenic (pronounced /ˈɑːrsənɪk/, *ARS-ə-nik*; also /ɑːrˈsɛnɪk/, *ar-SEN-ik* when attributive) is the chemical element that has the symbol *As*, atomic number 33 and atomic mass 74.92. Arsenic was first documented by Albertus Magnus in 1250.^[4] Arsenic is a notoriously poisonous metalloid with many allotropic forms, including a yellow (molecular non-metallic) and several black and grey forms (metalloids). Three metalloid forms of arsenic, each with a different crystal structure, are found free in nature (the minerals arsenic *sensu stricto* and the much rarer arsenolamprite and pararsenolamprite). However, it is more commonly found as arsenide and in arsenate compounds, several hundred of which are known. Arsenic and its compounds are used as pesticides, herbicides, insecticides and in various alloys.

Contents

- 1 History
- 2 Characteristics
 - 2.1 Isotopes
 - 2.2 Allotropes
 - 2.3 Chemical
 - 2.4 Compounds
 - 2.5 Occurrence
- 3 Production
- 4 Applications
 - 4.1 Wood preservation
 - 4.2 Medical
 - 4.3 Pigments
 - 4.4 Military
 - 4.5 Other uses
- 5 Biological role
- 6 Safety
 - 6.1 Arsenic in drinking water
 - 6.2 Occupational exposures
- 7 See also
- 8 References
- 9 External links

History

The word *arsenic* was borrowed from the Persian word زرنيق *Zarnikh*, meaning "yellow orpiment", into Greek as *arsenikon* (Ἀρσενικόν). It is also related to the similar Greek word "arsenikos" (Ἀρσενικός), meaning "masculine" or "potent". Arsenic sulfides (orpiment, realgar) and oxides have been known and used since ancient times.^[5] Zosimos (circa 300 AD) describes roasting *sandarach* (realgar) to obtain *cloud of arsenic* (arsenious oxide) which he then reduces to metallic arsenic.^[6] As the symptoms of arsenic poisoning were somewhat ill-defined, it was frequently used for murder until the advent of the Marsh test, a sensitive chemical test for its presence. (Another less sensitive but more general test is the Reinsch test.) Owing to its use by the ruling class to murder one another and its potency and discreetness, arsenic has been called the *Poison of Kings* and the *King of Poisons*.^[7]

During the Bronze Age, arsenic was often included in bronze, which made the alloy harder (so-called "arsenical bronze"). Albertus Magnus (Albert the Great, 1193–1280) is believed to have been the first to isolate the element in 1250 by heating soap together with arsenic trisulfide.^[4] In 1649, Johann Schröder published two ways of preparing arsenic.



Alchemical symbol for arsenic

Cadet's fuming liquid (impure cacodyl), the first organometallic compound, was synthesized in 1760 by Louis Claude Cadet de Gassicourt by the reaction of potassium acetate with arsenic trioxide.^[8]

In the Victorian era, "arsenic" (colourless, crystalline, soluble "white arsenic" trioxide) was mixed with vinegar and chalk and eaten by women to improve the complexion of their faces, making their skin paler to show they did not work in the fields. Arsenic was also rubbed into the faces and arms of women to "improve their complexion". The accidental use of arsenic in the adulteration of foodstuffs led to the Bradford sweet poisoning in 1858, which resulted in

approximately 20 deaths and 200 people taken ill with arsenic poisoning.^[9]

Characteristics

Isotopes

Main article: Isotopes of arsenic

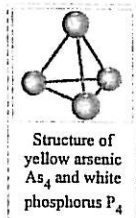
Naturally occurring arsenic is composed of one stable isotope, ⁷⁵As.^[10] As of 2003, at least 33 radioisotopes have also been synthesized, ranging in atomic mass from 60 to 92. The most stable of these is ⁷³As with a half-life of 80.3 days. Isotopes that are lighter than the stable ⁷⁵As tend to decay by β⁺ decay, and those that are heavier tend to decay by β[−] decay, with some exceptions.

At least 10 nuclear isomers have been described, ranging in atomic mass from 66 to 84. The most stable of arsenic's isomers is ^{68m}As with a half-life of 111 seconds.^[10]

germanium ← arsenic → selenium						
P			33As			
↑ As ↓ Sb	Periodic table					
Appearance						
metallic grey						
						
General properties						
Name, symbol, number	arsenic, As, 33					
Element category	metalloid					
Group, period, block	15, 4, p					
Standard atomic weight	74.92160(2) g·mol ^{−1}					
Electron configuration	[Ar] 4s ² 3d ¹⁰ 4p ³					
Electrons per shell	2, 8, 18, 5 (Image)					
Physical properties						
Phase	solid					
Density (near r.t.)	5.727 g·cm ^{−3}					
Liquid density at m.p.	5.22 g·cm ^{−3}					
Sublimation point	887 K, 615 °C, 1139 °F					
Triple point	1090 K (817°C), 3628 ^[1] kPa					
Critical point	1673 K, 7 MPa					
Heat of fusion	(grey) 24.44 kJ·mol ^{−1}					
Heat of vaporization	? 34.76 kJ·mol ^{−1}					
Specific heat capacity	(25 °C) 24.64 J·mol ^{−1} ·K ^{−1}					
Vapor pressure						
P/Pa	1	10	100	1 k	10 k	100 k
at 77K	553	596	646	706	781	874
Atomic properties						
Oxidation states	5, 3, 2, 1, ^[2] −3 (mildly acidic oxide)					
Electronegativity	2.18 (Pauling scale)					
Ionization energies (more)	1st: 947.0 kJ·mol ^{−1}					
	2nd: 1798 kJ·mol ^{−1}					
	3rd: 2735 kJ·mol ^{−1}					
Atomic radius	119 pm					
Covalent radius	119±4 pm					
Van der Waals radius	185 pm					
Miscellanea						
Crystal structure	rhombohedral					
Magnetic ordering	diamagnetic ^[3]					
Electrical resistivity	(20 °C) 333 nΩ·m					
Thermal conductivity	(300 K) 50.2 W·m ^{−1} ·K ^{−1}					
Young's modulus	8 GPa					
Bulk modulus	22 GPa					
Mohs hardness	3.5					
Brinell hardness	1440 MPa					
CAS registry number	7440-38-2					
Most stable isotopes						
Main article: Isotopes of arsenic						
iso	NA	half-life	DM	DE (MeV)	DP	
⁷³ As	syn	80.3 d	e	-	⁷³ Ge	
			γ	0.05D, 0.01D, e	-	
⁷⁴ As	syn	17.78 d	e	-	⁷⁴ Ge	
			β ⁺	0.941	⁷⁴ Ge	

A-36

Allotropes



Like phosphorus, arsenic is an excellent example of an element that exhibits allotropy, as its various allotropes have strikingly different properties. The three most common allotropes are *metallic grey*, *yellow* and *black arsenic*.^[11]

The most common allotrope of arsenic is *grey arsenic*. It has a similar structure to black phosphorus (β -metallic phosphorus) and has a layered crystal structure somewhat resembling that of graphite. It consists of many six-membered rings which are interlinked. Each atom is bound to three other atoms in the layer and is coordinated by each 3 arsenic atoms in the upper and lower layer. This relatively close packing leads to a high density of 5.73 g/cm^3 .^[12]

Yellow arsenic (As_4) is soft and waxy, not unlike P_4 . Both have four atoms arranged in a tetrahedral structure in which each atom is bound to the other three atoms by a single bond, resulting in very high ring strain and instability. This form of arsenic is the least stable, most reactive, more volatile, less dense, and more toxic than the other allotropes. Yellow arsenic is produced by rapid cooling of arsenic vapour with liquid nitrogen. It is rapidly

transformed into the grey arsenic by light. The yellow form has a density of 1.97 g/cm^3 .^[12]

Black arsenic is similar in structure to red phosphorus.^[12]

Chemical

The most common oxidation states for arsenic are -3 (arsenides: usually alloy-like intermetallic compounds), +3 (arsenates(III) or arsenites, and most organoarsenic compounds), and +5 (arsenates: the most stable inorganic arsenic oxycompounds). Arsenic also bonds readily to itself, forming square As_4^{2-} ions in the arsenide skutterudite. In the +3 oxidation state, the stereochemistry of arsenic is affected by the presence of a lone pair of electrons.

Arsenic is very similar chemically to its predecessor in the Periodic Table, phosphorus. Like phosphorus, it forms colourless, odourless, crystalline oxides As_2O_3 and As_2O_5 which are hygroscopic and readily soluble in water to form acidic solutions. Arsenic(V) acid is a weak acid. Like phosphorus, arsenic forms an unstable, gaseous hydride: arsine (AsH_3). The similarity is so great that arsenic will partly substitute for phosphorus in biochemical reactions and is thus poisonous. However, in subtoxic doses, soluble arsenic compounds act as stimulants, and were once popular in small doses as medicine by people in the mid 18th century.^[12]

When heated in air, arsenic oxidizes to arsenic trioxide; the fumes from this reaction have an odour resembling garlic. This odour can be detected on striking arsenide minerals such as arsenopyrite with a hammer. Arsenic (and some arsenic compounds) sublimates upon heating at atmospheric pressure, converting directly to a gaseous form without an intervening liquid state. The liquid state appears at 20 atmospheres and above, which explains why the melting point is higher than the boiling point.^[12]

Compounds

See also: Arsenic compounds

Arsenic compounds resemble in many respects those of phosphorus as both arsenic and phosphorus occur in the same group (column) of the periodic table.

The most important compounds of arsenic are arsenic(III) oxide, As_2O_3 , ("white arsenic"), the yellow sulfide orpiment (As_2S_3) and red realgar (As_4S_4), Paris Green, calcium arsenate, and lead hydrogen arsenate. The latter three have been used as agricultural insecticides and poisons.

Whilst arsenic trioxide forms during oxidation of arsenic, arsenic pentoxide is formed by the dehydration of arsenic acid. Both oxides dissolve in strong alkaline solution, with the formation of arsenite AsO_3^{3-} and arsenate AsO_4^{3-} respectively. The protonation steps between the arsenate and arsenic acid are similar to those between phosphate and phosphoric acid. However, arsenite and arsenous acid contain arsenic bonded to three oxygen and not hydrogen atoms, in contrast to phosphite and phosphorous acid (more accurately termed 'phosphonic acid'), which contain non-acidic P-H bonds. Arsenous acid is genuinely tribasic, whereas phosphonic acid is not.

A broad variety of sulfur compounds of arsenic are known, As_4S_3 , As_4S_4 , As_2S_3 and As_4S_{10} . All arsenic(III) halogen compounds (except with astatine) are known and stable. For the arsenic(V) compounds the situation is different: only the arsenic pentafluoride is stable at room temperature. Arsenic pentachloride is only stable at temperatures below -50°C and the pentabromide and pentaiodide are unknown.^[12]

Arsenic is used as group 5 element as part of the III-V semiconducting compounds. Gallium arsenide, indium arsenide and aluminium arsenide are used as semiconductor material when the properties of silicon are not suitable for the application and the higher price of the compounds is acceptable. Other arsenic compounds include:

- Arsenic acid (H_3AsO_4)
- Arsenous acid (H_3AsO_3)
- Arsenic trioxide (As_2O_3)
- Arsine (arsenic trihydride AsH_3)
- Cadmium arsenide (Cd_3As_2)
- Gallium arsenide (GaAs)
- Lead hydrogen arsenate (PbHAsO_4)

Arsenic also has a formal oxidation state of +2 in As_4S_4 , realgar. This is achieved by pairing As atoms to produce dimeric cations $[\text{As}-\text{As}]^{2+}$, so the total covalency of As is still in fact three.^[13]

Occurrence

See also: Arsenide minerals and Arsenate minerals



Arsenopyrite, also unofficially called mispickel,^[14] (FeAsS) is the most common arsenic-bearing mineral. In the lithosphere, the minerals of the formula M(II)AsS , with M(II) being mostly Fe, Ni and Co, are the dominant arsenic minerals.

Orpiment and realgar were formerly used as painting pigments, though they have fallen out of use owing to their toxicity and reactivity. Although arsenic is sometimes found native in nature, its main economic source is the mineral arsenopyrite mentioned above; it is also found in arsenides of metals such as silver, cobalt (cobaltite: CoAsS and skutterudite: CoAs_3) and nickel, as sulfides, and when oxidised as arsenate minerals such as mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ and erythrite, $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, and more rarely arsenites ('arsenite' = arsenate(III), AsO_3^{3-} as opposed to arsenate (V), AsO_4^{3-}).



Realgar

B-37

A large sample of native arsenic.

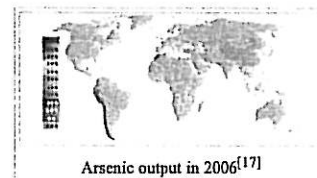
In addition to the inorganic forms mentioned above, arsenic also occurs in various organic forms in the environment.^[15]

Other naturally occurring pathways of exposure include volcanic ash, weathering of the arsenic-containing mineral and ores as well as groundwater. It is also found in food, water, soil and air.^[16]

Production

In 2005, China was the top producer of white arsenic with almost 50% world share, followed by Chile, Peru and Morocco, reports the British Geological Survey and the United States Geological Survey.^[17] The arsenic was recovered mostly during mining operations, for example the production from Peru comes mostly from copper mining and the production in China is owing to gold mining. Arsenic is part of the smelter dust from copper, gold, and lead smelters.^[18]

On roasting in air of arsenopyrite, arsenic sublimates as arsenic (III) oxide leaving iron oxides^[15], while roasting without air results in the production of metallic arsenic. Further purification from sulfur and other chalcogens is achieved by sublimation in vacuum or in a hydrogen atmosphere or by distillation from molten lead-arsenic mixture.^[19]



Applications

Wood preservation

The toxicity of arsenic to insects, bacteria, and fungi led to its use as a wood preservative. In the 1950s a process of treating wood with chromated copper arsenate (also known as CCA or Tanalith) was invented, and for decades this treatment was the most extensive industrial use of arsenic. Due to improved understanding of arsenic's high level of toxicity, most countries banned the use of CCA in consumer products. The European Union and United States led this ban, beginning in 2004.^{[20][21]}

As of 2002, US-based industries consumed 19,600 metric tons of arsenic. 90% of this was used for treatment of wood with CCA. In 2007, 50% of the 5,280 metric tons of consumption was still used for this purpose.^{[18][22]} In the United States, the use of arsenic in consumer products was discontinued for residential and general consumer construction on December 31, 2003 and alternative chemicals are now used, such as ACQ, borates, copper azole, cyproconazole, and propiconazole.^[23]

Although discontinued, this application is also one of the most concern to the general public. The vast majority of older pressure-treated wood was treated with CCA. CCA lumber is still in widespread use in many countries, and was heavily used during the latter half of the 20th century as a structural and outdoor building material. Although the use of CCA lumber was banned in many areas after studies showed that arsenic could leach out of the wood into the surrounding soil (from playground equipment, for instance), a risk is also presented by the burning of older CCA timber. The direct or indirect ingestion of wood ash from burnt CCA lumber has caused fatalities in animals and serious poisonings in humans; the lethal human dose is approximately 20 grams of ash. Scrap CCA lumber from construction and demolition sites may be inadvertently used in commercial and domestic fires. Protocols for safe disposal of CCA lumber do not exist evenly throughout the world; there is also concern in some quarters about the widespread landfill disposal of such timber.^[24]

Medical

During the 18th, 19th, and 20th centuries, a number of arsenic compounds have been used as medicines, including arsphenamine (by Paul Ehrlich) and arsenic trioxide (by Thomas Fowler). Arsphenamine as well as Neosalvarsan was indicated for syphilis and trypanosomiasis, but has been superseded by modern antibiotics. Arsenic trioxide has been used in a variety of ways over the past 500 years, but most commonly in the treatment of cancer. The US Food and Drug Administration in 2000 approved this compound for the treatment of patients with acute promyelocytic leukemia that is resistant to ATRA.^[25] It was also used as Fowler's solution in psoriasis.^[26] Recently new research has been done in locating tumours using arsenic-74 (a positron emitter). The advantages of using this isotope instead of the previously used iodine-124 is that the signal in the PET scan is clearer as the iodine tends to transport iodine to the thyroid gland producing a lot of noise.^[27]

Pigments

Copper acetoarsenite was used as a green pigment known under many different names, including 'Paris Green' and 'Emerald Green'. It caused numerous arsenic poisonings. Scheele's Green, a copper arsenate, was used in the 19th century as a colouring agent in sweets.^[28]

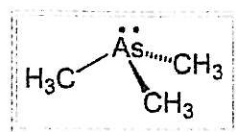
Military

After World War I the United States built up a stockpile of 20,000 tons of lewisite; a chemical weapon, acting as a vesicant (blister agent) and lung irritant. The stockpile was neutralized with bleach and dumped into the Gulf of Mexico after the 1950s.^[29] During the Vietnam War the United States used Agent Blue (a mixture of sodium cacodylate) and dimethyl arsine acid (cacodylic acid) as one of the rainbow herbicides to deprive the Vietnamese of valuable crops.

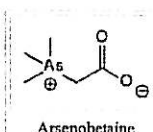
Other uses

- Various agricultural insecticides, termination and poisons. For example Lead hydrogen arsenate was used well into the 20th century as an insecticide on fruit trees.^[30] Its use sometimes resulted in brain damage to those working the sprayers. In the last half century, monosodium methyl arsenate (MSMA) and disodium methyl arsenate (DSMA), a less toxic organic form of arsenic, has replaced lead arsenate's role in agriculture.
- Used in animal feed, particularly in the US as a method of disease prevention^{[31][32]} and growth stimulation. One example is roxarsone which was used by 69.8 and 73.9% of the broiler starter and growers between 1995 to 2000.^[33]
- Gallium arsenide is an important semiconductor material, used in integrated circuits. Circuits made using the compound are much faster (but also much more expensive) than those made in silicon. Unlike silicon it is direct bandgap, and so can be used in laser diodes and LEDs to directly convert electricity into light.
- Also used in bronzing and pyrotechnics.
- Up to 2% of arsenic is used in lead alloys for lead shots and bullets.^[34]
- Arsenic is added in small quantities to brass to make it dezincification resistant. This grade of brass is used to make plumbing fittings.
- Arsenic is also used for taxonomic sample preservation.

Biological role



Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolised to less toxic forms of arsenic through a process of methylation. For example, the mold *Scopulariopsis brevicaulis* produce significant amounts of trimethylarsine if inorganic arsenic is present.^[35] The organic compound arsenobetaine is found in some marine foods such as fish and algae, and also in mushrooms in larger concentrations. The average person's intake is about 10–50 µg/day. Values about 1000 µg are not unusual following consumption of fish or mushrooms. But there is little danger in eating fish because this arsenic compound is nearly non-toxic.^[36]



Trimethylarsine

Some species of bacteria obtain their energy by oxidizing various fuels while reducing arsenate to arsenite. The enzymes involved are known as arsenate reductases (Arr).

In 2008, bacteria were discovered that employ a version of photosynthesis in the absence of oxygen with arsenites as electron donors, producing arsenates (just like ordinary photosynthesis uses water as electron donor, producing molecular oxygen). Researchers conjecture that historically these photosynthesizing organisms produced the arsenates that allowed the arsenate-reducing bacteria to thrive. One strain PHS-1 has been isolated and is related to the *γ*-Proteobacterium *Ectothiorhodospira shaposhnikovii*. The mechanism is unknown, but an encoded Arr enzyme may function in reverse to its known homologues.^[37]

Arsenic has been linked to epigenetic changes which are heritable changes in gene expression that occur without changes in DNA sequence and include DNA methylation, histone modification and RNA interference. Toxic levels of arsenic cause significant DNA hypermethylation of tumour suppressor genes p16 and p53 thus increasing risk of carcinogenesis. These epigenetic events have been observed in *in vitro* studies with human kidney cells and *in vivo* tests with rat liver cells and peripheral blood leukocytes in humans.^[38] Inductive coupled plasma mass spectrometry (ICP-MS) is used to detect precise levels of intracellular of arsenic and its other bases involved in epigenetic modification of DNA.^[39] Studies investigating arsenic as an epigenetic factor will help in developing precise biomarkers of exposure and susceptibility.

Safety

Main articles: Arsenic poisoning and Arsenic toxicity



Arsenic and many of its compounds are especially potent poisons. Arsenic disrupts ATP production through several mechanisms. At the level of the citric acid cycle, arsenic inhibits lipoic acid which is a cofactor for pyruvate dehydrogenase; and by competing with phosphate it uncouples oxidative phosphorylation, thus inhibiting energy-linked reduction of NAD⁺, mitochondrial respiration, and ATP synthesis. Hydrogen peroxide production is also increased, which might form reactive oxygen species and oxidative stress. These metabolic interferences lead to death from multi-system organ failure, probably from necrotic cell death, not apoptosis. A post mortem reveals brick red coloured mucosa, owing to severe haemorrhage. Although arsenic causes toxicity, it can also play a protective role.^[40]

Elemental arsenic and arsenic compounds are classified as "toxic" and "dangerous for the environment" in the European Union under directive 67/548/EEC. The International Agency for Research on Cancer (IARC) recognizes arsenic and arsenic compounds as group 1 carcinogens, and the EU lists arsenic trioxide, arsenic pentoxide and arsenate salts as category 1 carcinogens.

Arsenic is known to cause arsenicosis owing to its manifestation in drinking water, "the most common species being arsenate [HAsO_4^{2-} ; As(V)] and arsenite [H_3AsO_3 ; As(III)]". The ability of arsenic to undergo redox conversion between As(III) and As(V) makes its availability in the environment more abundant. According to Croal, Gralnick, Malasam, and Newman, "[the] understanding [of] what stimulates As(III) oxidation and/or limits As(V) reduction is relevant for bioremediation of contaminated sites (Croal). The study of chemolithoautotrophic As(III) oxidizers and the heterotrophic As(V) reducers can help the understanding of the oxidation and/or reduction of arsenic."^[41]

Treatment of chronic arsenic poisoning is easily accomplished. British anti-lewisite (dimercaprol) is prescribed in dosages of 5 mg/kg up to 300 mg each 4 hours for the first day. Then administer the same dosage each 6 hours for the second day. Then prescribe this dosage each 8 hours for eight additional days.^[42]

Arsenic in drinking water

Main article: Arsenic contamination of groundwater

Arsenic contamination of groundwater has led to a massive epidemic of arsenic poisoning in Bangladesh^[43] and neighbouring countries. Presently 42 major incidents around the world have been reported on groundwater arsenic contamination. It is estimated that approximately 57 million people are drinking groundwater with arsenic concentrations elevated above the World Health Organization's standard of 10 parts per billion. However, a study of cancer rates in Taiwan^[44] suggested that significant increases in cancer mortality appear only at levels above 150 parts per billion. The arsenic in the groundwater is of natural origin, and is released from the sediment into the groundwater owing to the anoxic conditions of the subsurface. This groundwater began to be used after local and western NGOs and the Bangladeshi government undertook a massive shallow tube well drinking-water program in the late twentieth century. This program was designed to prevent drinking of bacterially contaminated surface waters, but failed to test for arsenic in the groundwater. Many other countries and districts in South East Asia, such as Vietnam, Cambodia, and China have geological environments conducive to generation of high-arsenic groundwaters. Arsenicosis was reported in Nakhon Si Thammarat, Thailand in 1987, and the dissolved arsenic in the Chao Phraya River is suspected of containing high levels of naturally occurring arsenic, but has not been a public health problem owing to the use of bottled water.^[45]

In the United States, arsenic is most commonly found in the ground waters of the southwest.^[46] Parts of New England, Michigan, Wisconsin, Minnesota and the Dakotas are also known to have significant concentrations of arsenic in ground water. Increased levels of skin cancer have been associated with arsenic exposure in Wisconsin, even at levels below the 10 part per billion drinking water standard.^[47] According to a recent film funded by the US Superfund, millions of private wells have unknown arsenic levels, and in some areas of the US, over 20% of wells may contain levels that exceed established limits.^[48]

Low-level exposure to arsenic at concentrations found commonly in US drinking water compromises the initial immune response to H1N1 or swine flu infection according to NIEHS-supported scientists. The study, conducted in laboratory mice, suggests that people exposed to arsenic in their drinking water may be at increased risk for more serious illness or death in response to infection from the virus.^[49]

Epidemiological evidence from Chile shows a dose dependent connection between chronic arsenic exposure and various forms of cancer, particularly when other risk factors, such as cigarette smoking, are present. These effects have been demonstrated to persist below 50 parts per billion.^[50]

Analyzing multiple epidemiological studies on inorganic arsenic exposure suggests a small but measurable risk increase for bladder cancer at 10 parts per billion.^[51] According to Peter Ravenscroft of the Department of Geography at the University of Cambridge,^[52] roughly 80 million people worldwide consume between 10 and 50 parts per billion arsenic in their drinking water. If they all consumed exactly 10 parts per billion arsenic in their drinking water, the previously cited multiple epidemiological study analysis would predict an additional 2,000 cases of bladder cancer alone. This represents a clear underestimate of the overall impact, since it does not include lung or skin cancer, and explicitly underestimates the exposure. Those exposed to levels of arsenic above the current WHO standard should weigh the costs and benefits of arsenic remediation.

Early (1973) evaluations of the removal of dissolved arsenic by drinking water treatment processes demonstrated that arsenic is very effectively removed by co-precipitation with either iron or aluminum oxides. The use of iron as a coagulant, in particular, was found to remove arsenic with efficiencies exceeding 90%.^{[53][54]} Several adsorptive media systems have been approved for point-of-service use in a study funded by the United States Environmental Protection Agency (U.S.EPA) and the National Science Foundation (NSF). A team of European and Indian scientists and engineers have set up six arsenic treatment plants in West Bengal based on in-situ remediation method (SAR Technology). This technology does not use any chemicals and arsenic is left as an insoluble form (+5 state) in the subterranean zone by recharging aerated water into the aquifer and thus developing an oxidation zone to support arsenic oxidizing micro-organisms. This process does not produce any waste stream or sludge and is relatively cheap.^[55]

Magnetic separations of arsenic at very low magnetic field gradients have been demonstrated in point-of-use water purification with high-surface-area and monodisperse magnetite (Fe_3O_4) nanocrystals. Using the high specific surface area of Fe_3O_4 nanocrystals the mass of waste associated with arsenic removal from water has been

dramatically reduced.^[56]

Epidemiological studies have suggested a correlation between chronic consumption of drinking water contaminated with arsenic and the incidence of type 2 diabetes. However, the literature provides insufficient scientific evidence to show cause and effect between arsenic and the onset of diabetes mellitus type 2.

Occupational exposures

Main article: Arsenic poisoning

Industries that use inorganic arsenic and its compounds include wood preservation, glass production, nonferrous metal alloys, and electronic semiconductor manufacturing. Inorganic arsenic is also found in coke oven emissions associated with the smelter industry.^[57] Occupational exposure and poisoning may occur in persons working in these industries.

See also

- Aqua Tofana
- Arsenic poisoning
- Fowler's solution
- Grainger challenge
- White arsenic
- Arsenic trioxide

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External links

- CTD's Arsenic page and CTD's Arsenicals page from the Comparative Toxicogenomics Database
- A Small Dose of Toxicology
- ATSDR - Case Studies in Environmental Medicine: Arsenic Toxicity
- Contaminant Focus: Arsenic by the EPA.
- Environmental Health Criteria for Arsenic and Arsenic Compounds, 2001 by the WHO.
- Evaluation of the carcinogenicity of arsenic and arsenic compounds by the IARC.
- National Institute for Occupational Safety and Health - Arsenic Page
- National Pollutant Inventory - Arsenic
- origen.net – CCA wood and arsenic: toxicological effects of arsenic
- WebElements.com – Arsenic

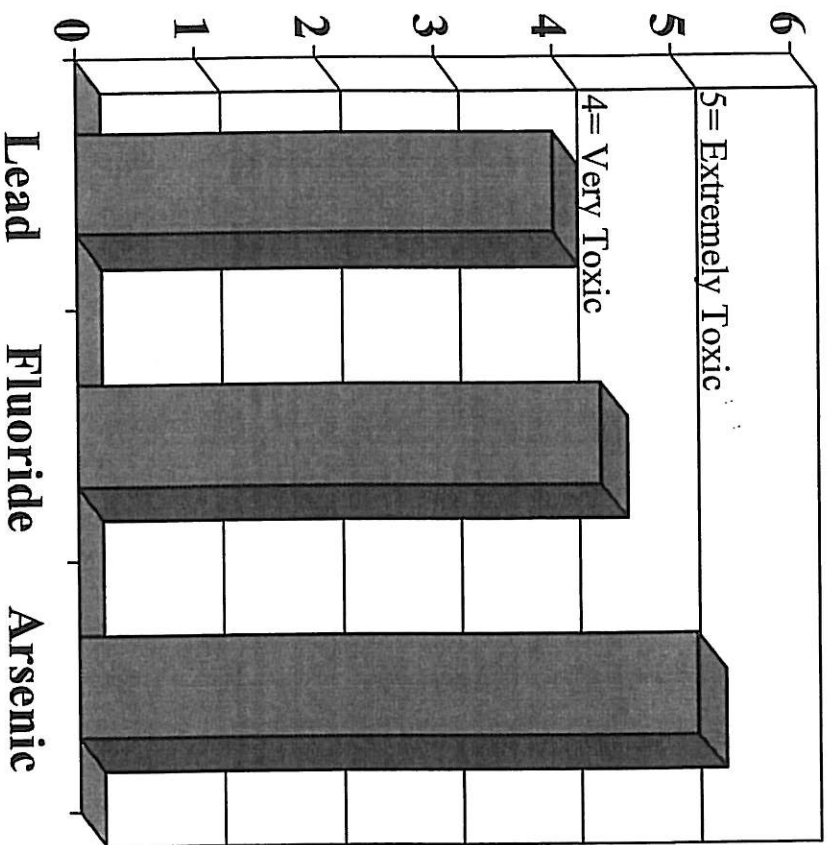
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Categories: Metalloids | Pnictogens | Toxicology | Chemical elements | Arsenic | Occupational safety and health | IARC Group 1 carcinogens | Biology and pharmacology of chemical elements

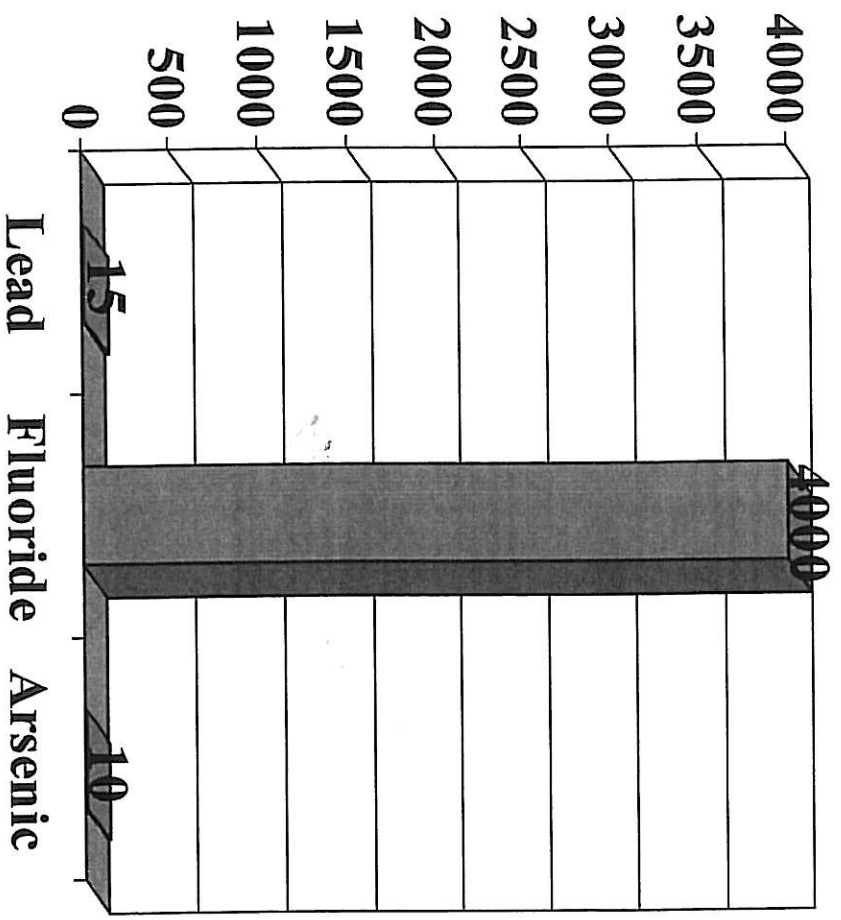
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How Toxic is Fluoride compared to Lead & Arsenic.

Relative Toxicity



EPA Maximum Contaminant Levels



Source: Clinical Toxicology of Commercial Products LD50 data - 1984

ppb (Parts per Billion)

James Robert Deal

From: Stark, Blake [Stark@nsf.org]
Sent: Tuesday, July 15, 2008 12:55 PM
To: James Robert Deal
Subject: FW: need your help (fluoride issue)

As indicated in the fluoride fact sheet, NSF Standard 60 references the US EPA MCL for fluoride. You may be able to obtain toxicology studies from the US EPA or through their website.

Thank you,

-Blake Stark, NSF

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From: James Robert Deal [mailto:JamesRobertDeal@jamesdeal.com]
Sent: Fri 7/11/2008 11:23 PM
To: Stark, Blake
Subject: need your help

Your Fact Sheet on water fluoridation mentions toxicological studies. Where would I find these?

I am looking for an assay of fluoridation materials in the raw, before dilution 240,000 times down to 1 ppm. Where would I find such an assay?

Sincerely,

James Robert Deal, Mortgage Broker
510-LO-25472, 510-MB-25306
James@DealMortgage.net
Deal Mortgage Corporation
P.O. Box 2370
Lynnwood WA 98036
425-771-1110 telephone
425-776-8081 fax
888-999-2022 toll-free
www.DealMortgage.net

Hexafluorosilicic acid

From Wikipedia, the free encyclopedia
(Redirected from Fluorosilicic acid)

Hexafluorosilicic acid is the chemical compound with the formula H_2SiF_6 . Hexafluorosilicic acid refers to an equilibrium mixture with hexafluorosilicate anion (SiF_6^{2-}) in an aqueous solution or other solvents that contain strong proton donors^[1] at low pH.

Contents

- 1 Nature of hexafluorosilicic acid
- 2 Production and principal reactions
- 3 Uses
 - 3.1 Niche applications
- 4 Safety
- 5 References

Nature of hexafluorosilicic acid

Like several related compounds, hexafluorosilicic acid does not exist as a discrete species, that is, a material with the formula H_2SiF_6 has not been isolated. Acids described similarly include chloroplatinic acid, fluoroboric acid, and hexafluorophosphoric acid, and, more commonly, carbonic acid. Distillation of hexafluorosilicic acid solutions produces no molecules of H_2SiF_6 ; instead the vapor consists of HF, SiF_4 , and water. Aqueous solutions of H_2SiF_6 contain the hexafluorosilicate anion, SiF_6^{2-} and protonated water. In this octahedral anion, the Si-F bond distances are 1.71 Å.^[2]

Production and principal reactions

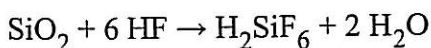
H_2SiF_6 is mainly produced as a by-product from the production of phosphoric acid from apatite and fluorapatite. In the U.S. about 85% of fluorspar is used to produce hydrofluorosilic acid.^[3] The

Dihydrogen hexafluorosilicate	
IUPAC name	Dihydrogen hexafluorosilicate (2-)
Other names	Hexafluorosilicic acid Hydrofluorosilic acid Fluorosilicic acid Fluosilicic acid Silicofluoride
Identifiers	
CAS number	16961-83-4 ✓
EC number	241-034-8
UN number	1778
RTECS number	VV8225000
Properties	
Molecular formula	H_2SiF_6
Molar mass	144.09 g/mol
Appearance	colourless solution
Density	1.22 g/cm ³ (25% soln.) 1.38 g/cm ³ (35% soln.) 1.46 g/cm ³ (61% soln.)
Melting point	ca. 19 °C (60–70% soln.) <- 30 °C (35& soln.)
Structure	
Molecular shape	Octahedral SiF_6^{2-}
Hazards	
MSDS	External MSDS
EU Index	009-011-00-5
EU classification	Corrosive (C)
R-phrases	R34
S-phrases	(S1/2), S26, S27, S45
Flash point	Non-flammable
Related compounds	
Related hexafluorosilicates	Ammonium hexafluorosilicate Sodium hexafluorosilicate Potassium hexafluorosilicate Magnesium hexafluorosilicate
Related compounds	Hexafluorophosphoric acid Fluoroboric acid
✓ (what is this?) (verify) Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)	

A-474

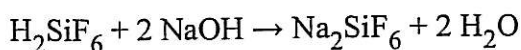
phosphoric and hydrofluoric acids are liberated from the mineral by the action of sulfuric acid. Some of the HF in turn reacts with silicate minerals, which are an unavoidable constituent of the mineral feedstock, to give silicon tetrafluoride. Thus formed, the silicon tetrafluoride reacts further with HF. The net process can be described as:^[4]

Infobox references

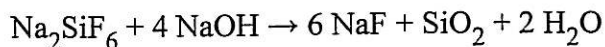


Hexafluorosilicic acid can also be produced by treating silicon tetrafluoride and hydrofluoric acid.

Neutralization of solutions of hexafluorosilicic acid with alkali metal bases produces the corresponding alkali metal fluorosilicate salts:

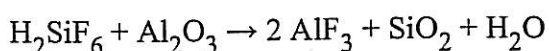


The resulting salt Na_2SiF_6 is mainly used in water fluoridation. Related ammonium and barium salts are produced similarly for other applications. With excess base, the hexafluorosilicate undergoes hydrolysis, so the neutralization of the hexafluorosilicic acid must guard against this easy hydrolysis reaction:



Uses

Hexafluorosilic acid is the feedstock for "virtually all organic and inorganic fluorine-bearing chemicals".^[3] The majority of the hexafluorosilicic acid is converted to aluminium fluoride and cryolite.^[4] These materials are central to the conversion of aluminium ore into aluminium metal. The conversion to aluminium trifluoride is described as:



Hexafluorosilicic acid is also converted to a variety of useful hexafluorosilicate salts. The potassium salt is used in the production of porcelains, the magnesium salt for hardened concretes, and the barium salts for phosphors.

Hexafluorosilicic acid is also commonly used for water fluoridation in several countries including the United States, Great Britain, and Ireland. In the U.S., about 40,000 tons of fluorosilic acid is recovered from phosphoric acid plants, and then used primarily in water fluoridation, sometimes after being processed into sodium silicofluoride.^[3]

Niche applications

H_2SiF_6 is a specialized reagent in organic synthesis for cleaving Si-O bonds of silyl ethers. It is more reactive for this purpose than HF. It reacts faster with t-butyldimethylsilyl (TBDMS) ethers than triisopropylsilyl (TIPS) ethers.^[5]

Hexafluorosilicic acid and the salts are used as wood preservation agents.^[6]

A-445

Safety

Hexafluorosilicic acid releases hydrogen fluoride when evaporated, so it has similar risks. It is corrosive and may cause fluoride poisoning; inhalation of the vapors may cause lung edema. Like hydrogen fluoride, it attacks glass and stoneware.^[7]

References

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<http://www.cdc.gov/niosh/ipcsneng/neng1233.html>

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Categories: [Hydrogen compounds](#) | [Fluorides](#) | [Silicates](#) | [Acids](#) | [Coordination compounds](#)

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A-46



STATE OF WASHINGTON
DEPARTMENT OF HEALTH
DIVISION OF ENVIRONMENTAL HEALTH
PO Box 47829 • Olympia, Washington 98504-7829

October 28, 2008

Dr. Eloise Kailin, MD
P.O. Box 1677
Sequim, WA 98382

Dear Dr. Kailin:

At the October 21, 2008 meeting of the Clallam County Board of Health you raised the question of whether or not the product used by the city of Port Angeles to fluoridate the city's water supply meets the regulatory requirements of the Washington State Department of Health. In follow-up we have confirmed that the city uses fluorosilicic acid provided from J. R. Simplot Company in Rock Springs, Wyoming. The product is NSF Standard 60 certified and does meet the requirements of our regulations.

At the Department of Health we do not have the resources that would allow us to do independent evaluations of water treatment products. As such we rely on national certification protocols to ensure the safety of water additives. Specifically, Washington Administrative Code 246-290-220 (3), requires that: "Any treatment chemicals, with the exception of commercially retailed hypochlorite compounds such as unscented Clorox, Purex, etc., added to water intended for potable use must comply with ANSI/NSF Standard 60. The maximum application dosage recommendation for the product certified by the ANSI/NSF Standard 60 shall not be exceeded in practice." Since the fluoridation product being used by the city of Port Angeles is certified under NSF Standard 60, the city's use of this product is in compliance with state law.

Attached is a July 2000 letter from Stan Hazan, general manager of the NSF Additives Certification Program, to US Representative Ken Calvert providing information on the NSF program. I hope you find this additional information useful.

Sincerely,

Gregg L. Grunenfelder, Assistant Secretary

Cc: Mary Selecky, Secretary of Health
Tom Locke, Clallam County Health Officer
Denise Clifford, Director Office of Drinking Water

B-47



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 2 1998

OFFICE OF
WATER

George C. Glasser
3016 23rd Street N.
St. Petersburg, FL 33713

Dear Mr. Glasser:

Your March 4, 1998, letter to Carol Browner regarding the need for research on fluorosilic acid was forwarded to the Health and Ecological Criteria Division (HECD) of Office of Science and Technology (OST) at the Office of Water (OW). The Environmental Protection Agency (EPA) appreciates your interest in this matter.

In the United States, there are no Federal safety standards which are applicable to drinking water additives, including those intended for use in fluoridating water. In the past, the EPA assisted the States and public water systems through the issuance of advisory opinions on acceptability of many additive chemicals. However, the Federal advisory program was terminated on October 4, 1988, and EPA assisted in establishment of voluntary product standards at NSF International (NSF) in Ann Arbor, Michigan. *American National Standards Institute (ANSI/NSF Standard 60: Drinking Water Treatment Chemicals – Health Effects)* was developed at NSF by a consortium of representatives from utilities, government, manufacturers and the public health community. The first edition of the Standard was issued in 1988. Standard 60 applies to all direct additive chemicals for potable water including sodium fluoride, hydrofluosilicic acid and sodium fluosilicate. At the present time, both NSF and Underwriter's Laboratories (UL) evaluate additive products against Standard 60 criteria and publish a listing of those products that meet the requirements of the Standard. You can contact NSF or UL for information on specific fluosilicate products.

EPA does receive many requests for information on the fluosilicate additives. Accordingly, EPA is in the process of conducting a literature search and review of the data available on the health effects and chemistry of these materials. This project should also identify research needs. It is anticipated that the review of the available data will be completed by this coming Fall. EPA plans to use the data collected to prepare a fact sheet that can be sent to citizens, like yourself, who request information on the fluosilicate additives used in fluoridation. EPA will also share the information collected with the Chemical Manager for Fluoride at ATSDR and with NSF International.

If you have any further question on this matter, please feel free to contact Dr. Joyce Donohue at 202-260-1318.

Sincerely,

A handwritten signature in black ink, appearing to read "Tudor T. Davies", is written over a horizontal line.

Tudor T. Davies, Director
Office of Science and Technology

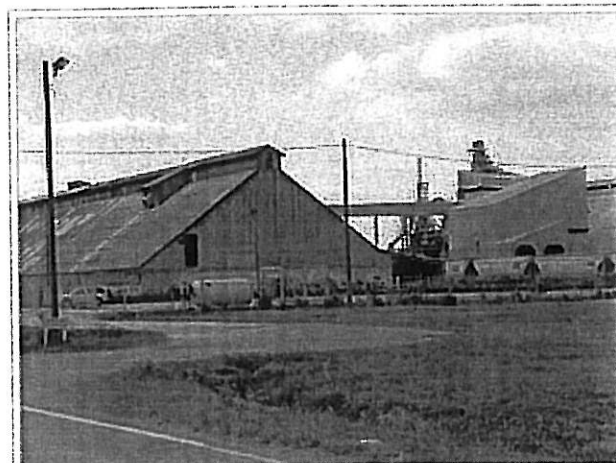
Bone Valley

From Wikipedia, the free encyclopedia
(Redirected from Bone valley)

The **Bone Valley** is a region of central Florida, encompassing portions of present-day Hardee, Hillsborough, Manatee, and Polk counties, in which phosphate is mined for use in the production of agricultural fertilizer. Florida currently contains the largest known deposits of phosphate in the United States.

Contents

- 1 Process
- 2 History
- 3 Rail Service
- 4 Risks of mining
- 5 External links



Phosphate fertilizer processing plant -- Nichols, Florida.

Process

Large walking draglines, operating twenty-four hours a day in surface mines, excavate raw pebble phosphate mixed with clay and sand (known as matrix) using huge buckets which can hold more than 40 cubic yards (30.58 m³) of earth. The matrix contains a number of chemical impurities, including naturally occurring uranium at concentrations of approximately 100 ppm.

The matrix is then dropped into a pit where it is mixed with water to create a slurry, which is then pumped through miles of large steel pipes to washing plants. These plants crush, sift, and separate the phosphate from the sand, clay, and other materials, and mix in more water to create a granular rock termed wetrock. The wetrock, which is typically of little use in raw form, is then moved largely by rail to fertilizer plants where it is processed. The final products include, but are not limited to, diammonium phosphate (DAP), monoammonium phosphate (MAP) and triple superphosphate (TSP).

Waste byproducts are stored in large phosphogypsum stacks and settling ponds, whose sizes are often measured in hundreds of acres, and can be up to 200 feet (60.96 m) tall in the case of large stacks. Phosphate processing produces significant amounts of fluorine gas, which must be treated by filtering through special scrubbers.

Most of the final product (known within the industry as 'dryrock') are then transported by rail to facilities along Tampa Bay, where they are transloaded onto ships destined for countries such as China.

Phosphate product intended for domestic use is assembled into long trains of covered hopper cars for



Rotary gondolas such as these are used by CSXT to transport phosphate rock from the Bone Valley region to transloading facilities along Tampa Bay -- Edison Junction, Florida.

northbound movement.

History

When the narrow gauge Florida Southern Railway reached Arcadia in 1886, it was only a sleepy little town and the builders paused only briefly before pushing the railroad south to Punta Gorda. Unknown to the railroad and the general public at this time, a great discovery had been made in 1881 by Captain Francis LeBaron of the United States Army Corps of Engineers, who was examining the lower Peace River area for the survey of a canal that would connect the headwaters of the Saint Johns River to Charlotte Harbor. Here he found and shipped to the Smithsonian Institution nine barrels of prehistoric fossils from the sand bars prevalent on the lower Peace River. He also noticed that there was a phosphatase quality to the fossils and the deposit they were found in was very valuable. The Smithsonian wanted him to return and lead an expedition for prospecting more fossils, but Captain LeBaron was unable to return due to his important duties at Fernandina where he was put in charge of harbor improvements.

Finally in December 1886, LeBaron was able to return to the Peace River where he dug some test pits and sent the samples to a laboratory for analysis. His suspicions were confirmed as the tests showed high quality bone phosphate of lime. LeBaron tried in vain to round up investors in New York, Boston and Philadelphia, but none were willing to invest in the project. Frustrated he left the United States for the ill-fated Nicaraguan Canal Project.

Meanwhile, the test results became known to Colonel G.W. Scott who owned the G.W. Scott Manufacturing Co. of Atlanta and he quickly sent a representative down to Arcadia who made several large purchases along the Peace River. Colonel T.S. Moorhead of Pennsylvania had also learned about the deposits from Captain LeBaron, but not the secret of their location, traveled to Arcadia where he luckily stumbled onto the famous sand bars. Mr. Moorhead formed the Arcadia Phosphate Company, with the Scott Mfg. Co. quickly agreeing to purchase the entire output. The very first shipment of Florida phosphate was made in May 1888 when the first ten car loads were dispatched to Scott's Fertilizer Works in Atlanta, Georgia. Soon after, G.W. Scott formed the Desoto Phosphate Co. at Zolfo where the Florida Southern Railway crossed the Peace River. However the biggest player was the Peace River Phosphate Co. (formed in January 1887) which was located in Arcadia by M.M. Knudson of New York and they quickly built a narrow gauge railroad from the works on the river to the interchange with the Florida Southern. It is this company and its railroad that is the first direct ancestor of the future Charlotte Harbor & Northern. The Peace River Phosphate Co. began mining in the Winter of 1889, and most of the ore was shipped to Punta Gorda via. the Florida Southern, where it was loaded onto boats for export to Europe.

Early mining methods was the pick and shovel method where the above water sand bars were mined by hand and loaded onto barges which were herded by shallow water tug boats to the drying works located nearby. Soon the use of suction dredges were put into use and the mining spread all along the lower Peace River.

Moorhead soon sold his Arcadia Phosphate Co. to Hammond & Hull of Savannah, Georgia a large fertilizer operation in that city. Moorhead then left Florida and returned to Pennsylvania, where he developed a phosphate mine in Juniata County, PA and formed the narrow gauge Tuscarora Valley Rail Road. Hammond & Hull also owned the Charlotte Harbor Phosphate Co. which had their works at Hull, connecting with the Florida Southern by a short branch line. Wanting to connect the two plants, Hammond & Hull built a narrow gauge railroad between Arcadia and Hull around 1890. The railroad served various load outs along the river where the barges full of pebble would be unloaded and raised to the railroad and loaded onto ore cars for the journey to the drying plants at Arcadia and Hull. Hammond

dropped out around 1890 and the new firm was known as Comer & Hull.

The Peace River Phosphate Co. in the mean time had built a narrow gauge railroad north of Arcadia to their load-outs along the Peace River. Like the Comer & Hull operations, the ore was hauled to the drying plant at Arcadia where it was loaded into the narrow gauge boxcars of the Florida Southern. When the railroad converted it's Charlotte Harbor Division to standard gauge in 1892, both the Peace River Phosphate Co. and Comer & Hull operations converted their respective railroads. Joseph Hull of Comer & Hull purchased a half interest in the Peace River Phosphate Co. about this time.

In December 1894, Joseph Hull consolidated the Arcadia Phosphate Co., Charlotte Harbor Phosphate Co., Desota Phosphate & Mining Co. & Peace River Phosphate Co. into the Peace River Phosphate Mining Co.

Peter Bradley of New York was one of the fertilizer capitalists (Bradley Fertilizer Co.) that Captain LeBaron had first approached about the sand bars, but was initially rebuffed. In May 1899, he was involved in the merger of 22 fertilizer companies into the American Agricultural Chemical Co. becoming vice president and a director of the new corporation.

AACC began buying the stock of the Peace River Phosphate Mining Co. beginning in June 1899 and finishing up in January 1902.

The Peace River Phosphate Mining Company Railroad consisted of a mainline running south from Arcadia to Liverpool. A few short branches connected the railroad to the Florida Southern (later the Plant System in 1896 and the ACL after 1902) at Arcadia, Hull and Liverpool. At Hull was the washing plant where sand was removed. Liverpool housed the drying plant and barge loading facilities. A branch running north for about 3 miles (4.8 km) upstream from Arcadia served the many load outs along the river.

In the early years, phosphate from the Peace River area was barged to Punta Gorda, or shipped by rail to Port Tampa. Other important ports were later established at Seddon Island, Boca Grande, and Rockport.

Today, there are two companies which mine phosphate rock in the region, Mosaic Inc. (formed from the merger of IMC-Global and Cargill Crop Nutrition) as well as CF Industries. At present, Mosaic is seeking to mine properties further south, in Hardee and Manatee Counties.

With renewed interest in corn-based Ethanol fuel, the demand for fertilizer is expected to increase.

Rail Service

Throughout most of the twentieth century, the Bone Valley region received service from two major railroads, the Atlantic Coast Line and Seaboard Air Line. More than a few plants and mines saw the services of *both* railroad companies, such as the Ridgewood fertilizer plant located at Bartow, and the massive Pierce complex south of Mulberry. It was not until the 1967 Seaboard Coast Line merger that the bitter rivalry was put to rest. SCL itself was later absorbed into CSX, who have since pursued an aggressive strategy of abandoning redundant trackage.



Phosphate train enroute to a fertilizer plant. --
Pierce, Florida.

Risks of mining

Phosphate is a declining export to China. Previously, significant

amounts of rock were shipped to China, where it was processed into phosphate fertilizer. The majority of phosphate mining in Florida is done in the Peace River watershed. Phosphate mining companies use draglines to remove surface soils up to 60 feet (18.29 m) deep over thousands of contiguous acres. Once land is mined, state law requires that it be reclaimed. Wetlands are reclaimed on an acre for acre, type for type basis. Most modern mining permits actually require companies to recreate more wetlands than were initially present on the land. More than 180,000 acres (728 km²) have already been mined and reclaimed in the Peace River watershed. As reserves in the northern portion of the bone valley are depleting, mining companies are now seeking permits for another 100,000 acres (405 km²), which will replace reclaimed mines to the north.



Phosphogypsum stack located near Fort Meade, Florida. These contain the waste byproducts of the phosphate fertilizer industry.

One byproduct of the extraction process is clay, which is stored in settling ponds and eventually comprise thirty to forty percent of a mine site. Some of these ponds can measure thousands of acres. Rain drains slower through these clay-laden ponds than typical soil. Critics argue that this, in turn, reduces baseflow to the Peace River. Some studies have indicated that reclaimed lands actually provide a more consistent baseflow because the sandier soils of the reclaimed land provide faster baseflow, while the clay provides a slower steady flow, creating more flow during dry periods than native land. Since the 1960s, the average annual flow of the middle Peace River has declined from 1,350 cubic feet (38.23 m³) to 800 cubic feet (22.65 m³) per second (38.23 to 22.65 m³/s). Critics argue that this flow reduction is due to phosphate mining, but studies by the Southwest Florida Water Management District have shown that the reduction in flow is due to multidecadal oscillation in Atlantic Ocean temperatures.

Critics argue that each holding pond has been perceived as a risk that threatens water quality, public health, wildlife, and the regional economy. Dams restraining the ponds have overflowed or burst, sending a slurry of clay into the river, and coating the riverbed for many miles with a toxic clay slime that suffocates flora and fauna. One such incident in 1971 killed over three million fish when two million gallons of phosphate waste swept into the river, causing an estimated five foot tall tide of slime that spread into adjacent pastures and wetlands. Since the 1971 spill, clay settling areas are now constructed as engineered dams. No such spills have occurred from any settling areas built to these standards. The current dams even withstood three hurricanes which crossed directly over the Bone Valley in 2004.

Most recently, in 2004, during Hurricane Frances, a phosphogypsum stack was overwhelmed by hurricane rains and the levees were breached, sending over 18,000 US gal (68,137 L) of acidic process water into Tampa Bay. Cargill Crop Nutrition, who owned the stack, added lime into the affected areas in an attempt to neutralize the highly-acidic runoff. Due to the extraordinary amount of runoff created by the hurricane, the spill was quickly diluted and environmental damage was minimal. In a consent agreement with the Department of Environmental Protection, Cargill greatly increased its water treatment capacity at the facility. The facility is a no discharge facility and was overwhelmed by the above normal rainfall in 2004, in addition to being affected by three hurricanes.

On occasion, clay slime spills have prevented the *Peace River Manasota Water Supply Authority* from using river flows for drinking water, forcing municipalities to seek water supplies elsewhere, or rely on stored supplies. On several occasions, the effects of heavy rainfall have created sinkholes beneath the settling ponds.

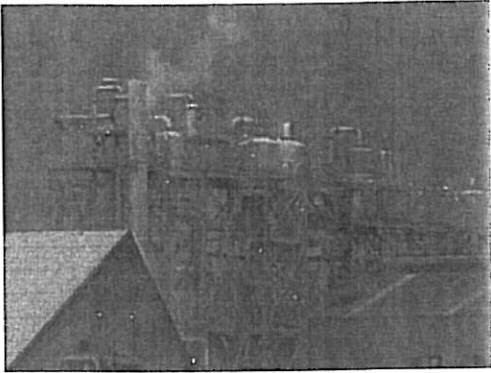
External links

- CF Industries, Inc.
- Mosaic Co.
- The Phosphate Fertilizer Industry: An Environmental Overview
- Florida Phosphate Facts

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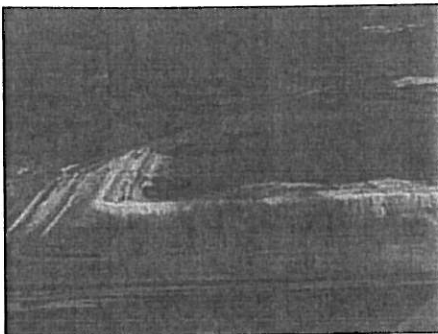
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Photographs of Gypsum Stacks w/ Wastewater Ponds

All of the photographs on this page, except for the photos of the sinkhole, were taken by Michael and Paul Connett in Central Florida (the heart of the phosphate industry) in June 2001. They can be copied and distributed freely. Click on the photos to access larger copies of each. To learn more about the phosphate fertilizer industry, [click here](#).

Phosphogypsum Stacks w/ Wastewater Ponds



Sinkhole in Gypsum Stacks

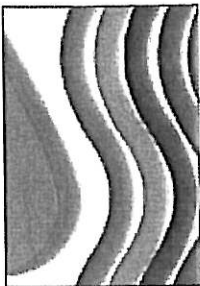


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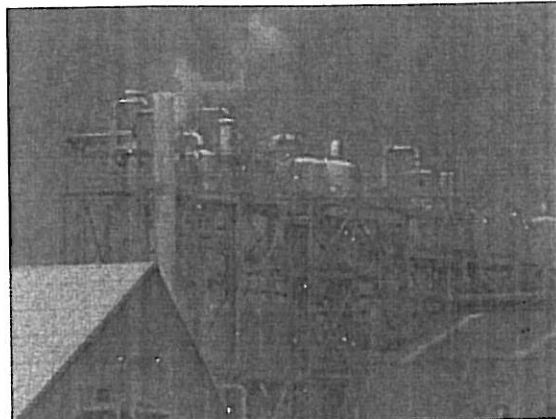
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IMC Agrico - Phosphate Processing Facility.
(Click to see more photographs)

The Phosphate Fertilizer Industry: An Environmental Overview

by Michael Connett
Fluoride Action Network
May 2003

- 1) [Introduction](#)
- 2) [Effects of Fluoride Pollution](#)
- 3) [Litigation from Fluoride Damage](#)
- 4) [Scrubbing away the problem](#)
- 5) [A Missed Opportunity: Little Demand for Silicofluorides](#)
- 6) [Fluoridation: "An ideal solution to a long-standing problem"?](#)
- 7) [Recent Findings on Silicofluorides](#)
- 8) [Gypsum Stacks & 'Slime Ponds'](#)
- 9) [Radiation Hazard](#)
- 10) [Will radioactive gypsum be added to roads?](#)
- 11) [Commercial Uranium Production](#)
- 12) [Cold War Secrets & Worker Health](#)
- 13) [Wastewater Issues](#)
- 14) [References](#)
- 15) [Photographs of the Phosphate Industry](#)
- 16) [Further Reading](#)

1) [Introduction](#) ([back to top](#))

They call them "wet scrubbers" - the pollution control devices used by the phosphate industry to capture fluoride gases produced in the production of commercial fertilizer.

In the past, when the industry let these gases escape, vegetation became scorched, crops destroyed, and cattle crippled.

Today, with the development of sophisticated air-pollution control technology, less of the fluoride escapes into the atmosphere, and the type of pollution that threatened the survival of some communities in the 1950s and 60s, is but a thing of the past (at least in the US and other wealthy countries).

B-56

However, the impacts of the industry's fluoride emissions are still being felt, although more subtly, by millions of people - people who, for the most part, do not live anywhere near a phosphate plant.

That's because, after being captured in the scrubbers, the fluoride acid (hydrofluorosilicic acid), a classified hazardous waste, is barreled up and sold, unrefined, to communities across the country. Communities add hydrofluorosilicic acid to their water supplies as the primary fluoride chemical for water fluoridation.

Even if you don't live in a community where fluoride is added to water, you'll still be getting a dose of it through cereal, soda, juice, beer and any other processed food and drink manufactured with fluoridated water.

Meanwhile, if the phosphate industry has its way, it may soon be distributing another of its by-products to communities across the country. That waste product is radium, which may soon be added to a roadbed near you - if the EPA buckles and industry has its way.

2) Effects of Fluoride Pollution ([back to top](#))

Central Florida knows it well. So too does Garrison Montana, Cubatao Brazil, and any other community where phosphate industries have had inefficient, or non-existent, pollution control: Fluoride.

The Canadian Broadcasting Corporation (CBC) called the phosphate industry a "pandora's box." That, while it brought wealth to rural communities, it also brought ecological devastation. The CBC described the effects of one particular phosphate plant in Dunville, Ontario:

"Farmers noticed it first... Something mysterious burned the peppers, burned the fruit, dwarfed and shriveled the grains, damaged everything that grew. Something in the air destroyed the crops. Anyone could see it... They noticed it first in 1961. Again in '62. Worse each year. Plants that didn't burn, were dwarfed. Grain yields cut in half...Finally, a greater disaster revealed the source of the trouble. A plume from a silver stack, once the symbol of Dunville's progress, spreading for miles around poison - fluorine. It was identified by veterinarians. There was no doubt. What happened to the cattle was unmistakable, and it broke the farmer's hearts. Fluorosis - swollen joints, falling teeth, pain until cattle lie down and die. Hundreds of them. The cause - fluorine poisoning from the air."

Fluoride has been, and remains to this day, one of the largest environmental liabilities of the phosphate industry. The source of the problem lies in the fact that raw phosphate ore contains high concentrations of fluoride, usually between 20,000 to 40,000 parts per million (equivalent to 2 to 4% of the ore).

When this ore is processed into water-soluble phosphate (via the addition of sulfuric acid), the fluoride content of the ore is vaporized into the air, forming highly toxic gaseous compounds (hydrogen fluoride and silicon tetrafluoride).

In the past, when the industry had little, if any, pollution control, the fluoride gases were frequently emitted in large volumes into surrounding communities, causing serious environmental damage.

In Polk County, Florida, the creation of multiple phosphate plants in the 1940s caused damage to nearly 25,000 acres of citrus groves and "mass fluoride poisoning" of cattle. It is estimated that, as a result of fluoride contamination, "the cattle population of Polk County dropped 30,000 head" between 1953 and 1960, and "an estimated 150,000 acres of cattle land were abandoned" (Linton 1970).

According to the former president of the Polk County Cattlemen's Association:

"Around 1953 we noticed a change in our cattle... We watched our cattle become gaunt and starved, their legs became deformed; they lost their teeth. Reproduction fell off and when a cow did have a calf, it was also affected by this malady or was a stillborn" (ibid).

In the 1960s, air pollution emitted by another phosphate plant in Garrison, Montana was severe enough to be branded "the worst in the nation" by a 1967 National Air Pollution Conference in Washington, D.C.

As in Polk County, and other communities downwind of fluoride emissions, the cattle in Garrison were poisoned by fluoride. As described in a 1969 article from *Good Housekeeping*:

"The blight had afflicted cattle too. Some lay in the pasture, barely able to move. Others limped and staggered on swollen legs, or painfully sank down and tried to graze on their knees... Ingested day after day, the excessive fluoride had caused tooth and bone disease in the cattle, so that they could not tolerate the anguish of standing or walking. Even eating or drinking was an agony. Their ultimate fate was dehydration, starvation - and death."

3) Litigation from Fluoride Damage ([back to top](#))

Damage to vegetation and livestock, caused by fluoride emissions from large industry, has resulted, as one might expect, in a great deal of expensive litigation. In 1983, Dr. Leonard Weinstein of Cornell University, stated that "certainly, there has been more litigation on alleged damage to agriculture by fluoride than all other pollutants combined" (Weinstein 1983). While Weinstein was referring to fluoride pollution in general, his comments give an indication of the problem facing the phosphate industry - one of the most notorious emitters of fluoride - in its early days.

So too does an estimate from Dr. Edward Groth, currently a Senior Scientist at Consumers Union. According to an article written by Groth, fluoride pollution between the years 1957 to 1968, "was responsible for more damage claims against industry than all twenty (nationally monitored air pollutants) combined."

The primary reason for the litigation against fluoride emitters was "the painful, economically disastrous, debilitating disease" that fluoride causes to livestock (Hodge & Smith 1977). As noted in a 1970 review by the US Department of Agriculture (USDA),

"Airborne fluorides have caused more worldwide damage to domestic animals than any other air pollutant" (Lillie 1970).

Another review on air pollution reached the same conclusion. According to Ender (1969):

"The most important problem concerning damage to animals by air pollution is, no doubt, the poisoning of domestic animals caused by fluorine in smoke, gas, or dust from various industries; industrial fluorosis in livestock is today a disorder well known by veterinarians in all industrialized countries."

According to a review discussing "Fluorine toxicosis and industry", Shupe noted that:

"Air pollution damage to agricultural production in the United States in 1967 was estimated at \$500,000,000. Fluoride damage to livestock and vegetation was a substantial part of this amount" (Shupe 1970).

4) Scrubbing away the problem ([back to top](#))

Due to the inevitable liabilities that fluoride pollution presented, and to an increasingly

stringent set of environmental regulations, the phosphate industry began cleaning up its act.

As noted by Ervin Bellack, a chemist for the US Public Health Service:

"In the manufacture of super-phosphate fertilizer, phosphate rock is acidulated with sulfuric acid, and the fluoride content of the rock evolves as volatile silicofluorides. In the past, much of this volatile material was vented to the atmosphere, contributing heavily to pollution of the air and land surrounding the manufacturing site. As awareness of the pollution problem increased, scrubbers were added to strip particulate and gaseous components from the waste gas..." (Bellack 1970)

A 1979 review, published in the journal *Phosphorous & Potassium*, added:

"The fluorine compounds liberated during the acidulation of phosphate rock are now rightly regarded as a menace and the industry is now obliged to suppress emissions-containing vapors to within very low limits in most parts of the world..."

In the past, little attention was paid to the emission of gaseous fluorine compounds in the fertilizer industry. But today fluorine recovery is increasingly necessary because of stringent environmental restrictions which demand drastic reductions in the quantities of volatile and toxic fluorine compounds emitted into the waste gases. These compounds now have to be recovered and converted into harmless by-products for disposal or, more desirably, into marketable products" (Denzinger 1979).

5) A Missed Opportunity: Little Demand for Silicofluorides [\(back to top\)](#)

Considering the great demand among big industry for fluoride chemicals as a material used in a wide variety of commercial products and industrial processes, the phosphate industry could have made quite a handsome profit selling its fluoride wastes to industry. This was indeed the hope among some industry analysts, including the authors of the review noted above (Denzinger 1979).

However, the US phosphate industry has thus far been unable to take advantage of this market. The principal reason for this failure stems from the fact that fluoride captured in the scrubbers is combined with silica. The resulting silicofluoride complex has, in turn, proved difficult for the industry to separate and purify in an economically-viable process.

As it now stands, silicofluoride complexes (hydrofluorosilicic acid & sodium silicofluoride) are of little use to industry.

Thus, while US industry continues to satisfy its growing demand for high-grade fluoride chemicals by importing calcium fluoride from abroad (primarily from Mexico, China, and South Africa), the phosphate industry continues dumping large volumes of fluoride into the acidic wastewater ponds that lie at the top of the mountainous waste piles which surround the industry.

In 1995, the Tampa Tribune summed up the situation as follows:

"The U.S. demand for fluorine, which was 400,000 tons, is expected to jump 25 percent by next year... Even though 600,000 tons of fluorine are contained in the 20 million tons of phosphate rock mined in Florida, the fluorine market has been inaccessible because the fluorine is tied up with silica, a hard, glassy material."

Of course, not all of the phosphate industry's fluoride waste is disposed of in the ponds. As noted earlier, the phosphate industry has found at least one regular

consumer of its silicofluorides: municipal water-treatment facilities.

According to recent estimates, the phosphate industry sells approximately 200,000 tons of silicofluorides (hydrofluorosilicic acid & sodium silicofluoride) to US communities each year for use as a water fluoridation agent (Coplan & Masters 2001).

6) Fluoridation: "An ideal solution to a long-standing problem"? ([back to top](#))

In 1983, Rebecca Hanmer, the Deputy Assistant Administrator for Water at the US Environmental Protection Agency, described the policy of using the phosphate industry's silicofluorides for fluoridation as follows:

"In regard to the use of fluosilicic acid as the source of fluoride for fluoridation, this agency regards such use as an ideal solution to a long standing problem. By recovering by-product fluosilicic acid from fertilizer manufacturing, water and air pollution are minimized, and water authorities have a low-cost source of fluoride available to them." ([See letter](#))

Another EPA official, Dr. J. William Hirzy, the current Senior Vice-President of EPA Headquarters Union, recently expressed a different view on the matter. According to Hirzy:

"If this stuff gets out into the air, it's a pollutant; if it gets into the river, it's a pollutant; if it gets into the lake it's a pollutant; but if it goes right into your drinking water system, it's not a pollutant. That's amazing... There's got to be a better way to manage this stuff" (Hirzy 2000).

7) Recent Findings on Silicofluorides ([back to top](#))

Adding to Hirzy's, and the EPA Union's, concerns are three recent findings.

First and foremost are two recent studies reporting a relationship between water treated with silicofluorides and elevated levels of lead in children's blood (Masters & Coplan 1999, 2000). The authors of these studies speculate that the silicofluoride complex may increase the uptake of lead (derived from other environmental sources, such as lead paint) into the bloodstream.

The second finding is the recent, and quite remarkable concession from the EPA, that despite 50 years of water fluoridation, the EPA has no chronic health studies on silicofluorides. All safety studies on fluoride to date have been conducted using pharmaceutical-grade sodium fluoride, not industrial-grade silicofluorides. A similar concession has also been obtained from the respective authorities in England.

The defense made by agencies promoting water fluoridation, such as the US Centers for Disease Control, to the lack of such studies, is that when the silicofluoride complex is diluted into water, it dissociates into free fluoride ions or other fluoride compounds (e.g. aluminum-fluoride), and thus the treated water, when consumed, will have no remaining silicofluoride residues (Urbansky & Schock, 2000).

This argument, while supported by a good deal of theoretical calculation is backed by a notable lack of laboratory data. Moreover, a recently obtained and translated PhD dissertation from a German chemist (Westendorf 1975) contradicts the claims. According to the dissertation, not only do the silicofluorides *not* fully dissociate, the remaining silicofluoride complexes are more potent inhibitors of cholinesterase, an enzyme vital to the functioning of the central nervous system.

The third finding, although perhaps of less concern, is that the silicofluorides, as obtained from the scrubbers of the phosphate industry, contain a wide variety of impurities present in the process water - including arsenic, lead, and possibly radionuclides. While these impurities occur at low concentrations, especially after dilution into the water, their purposeful addition to water supplies directly violates EPA

public health goals. For instance, the EPA's Maximum Contaminant Level Goal for arsenic, a known human carcinogen, is 0 parts per billion. However, according to the National Sanitation Foundation, the addition of silicofluorides to the water supply will add, on average, about 0.1 to 0.43 ppb, and as much as 1.6 ppb, arsenic to the water.

As noted by the Salt Lake Tribune,

"Those who had visions of sterile white laboratories when they voted for fluoride weren't thinking of fluorosilicic acid. Improbable as this sounds, much of it is recovered from the scrubbing solution that scours toxins from smokestacks at phosphate fertilizer plants."

8) Gypsum Stacks & 'Slime Ponds' ([back to top](#))

To make 1 pound of commercial fertilizer, the phosphate industry creates 5 pounds of contaminated phosphogypsum slurry (calcium sulfate). This slurry is piped from the processing facilities up into the acidic wastewater ponds that sit atop the mountainous waste piles known as gypsum stacks. ([See photos](#))

According to the EPA, 32 million tons of new gypsum waste is created each year by the phosphate industry in Central Florida alone. (Central Florida is the heart of the US phosphate industry). The EPA estimates that the current stockpile of waste in Central Florida's gypsum stacks has reached "nearly 1 billion metric tons." (The average gypsum stack takes up about 135 acres of surface area - equal to about 100 football fields - and can go as high as 200 feet.)

9) Radiation Hazard ([back to top](#))

It is sort of a misnomer, however, to call these stacks "gypsum" stacks. Indeed, if the stacks were simply gypsum, they probably wouldn't exist, as gypsum can be readily sold for various purposes (e.g. as a building material). What can't be readily sold, however, is radioactive gypsum, which is about the only type of gypsum the phosphate industry has to offer.

The source of the gypsum's radioactivity is the presence of uranium, and uranium's various decay products (i.e. radium), in raw, phosphate ore. As noted by the Sarasota Herald Tribune

"there is a natural and unavoidable connection between phosphate mining and radioactive material. It is because phosphate and uranium were laid down at the same time and in the same place by the same geological processes millions of years ago. They go together. Mine phosphate, you get uranium."

While uranium, and its decay-products, naturally occur in phosphate ore, their concentrations in the gypsum waste, after the extraction of soluble phosphate, are up to 60 times greater.

The gypsum has therefore been classified as a "Naturally Occurring Radioactive Material", or NORM waste, although some, including the EPA, have questioned whether this classification understates the problem. According to the Tampa Tribune, the gypsum "is among the most concentrated radioactive waste that comes from natural materials."

It is so concentrated, in fact, that "it can't be dumped at the one landfill in the country licensed to take only NORM waste."

Thus, according to US News & World Report, the EPA is currently "weighing whether to classify the gypsum stacks as hazardous waste under federal statutes, which would force the industry to provide strict safeguards" (to nearly 1 billion tons of waste).

One of EPA's main concerns with gypsum stacks centers around the fact that radium-

226 breaks down into radon gas. When radon gas is formed, it can become airborne, leading to potentially elevated exposures downwind of the stacks. Such airborne exposures are of particular concern to areas like Progress Village, Florida, where "a new gypsum stack is rising a few hundred yards from a grade school."

According to US News & World Report, there is evidence to suggest that cancer rates downwind of the stacks may be elevated. A 1995 article in the magazine stated:

"Some epidemiological studies suggest that lung cancer rates among nonsmoking men in the phosphate region are up to twice as high as the state average. Acute leukemia rates among adults are also double the average. An industry-sponsored study of male phosphate workers, however, found lung cancer rates no higher than the state average. There is no proof that mine wastes cause cancer, but the evidence is worrisome."

10) Will radioactive gypsum be added to roads? ([back to top](#))

With the growing realization that gypsum stacks represent a serious environmental threat to Central Florida, both now and for generations to come, the phosphate industry has been looking into ways of reducing the size of the stacks (and the size of their liability.)

In an interesting parallel to fluoride, the phosphate industry is looking to turn its gypsum waste into a marketable product: as a potential cover for landfills, as a soil conditioner, and as a base material for roads.

According to Robert Vanderslice, head of Phosphate Management for Florida's Department of Environmental Protection, the gypsum is a "good material to replace lime rock in roads. Lime rock will run out at some time, and we're still building a lot of roads. Building roads with phosphogypsum would consume quite a bit of gypsum."

In 1995, a "Phosphogypsum Fact-Finding Forum" organized by the Florida Institute of Phosphate Research, presented a "message aimed straight at Washington: Relax the rules on using gypsum and the mountains will gradually disappear."

As of yet, however, the EPA does not appear willing to relax its rules and lift its ban on commercial uses of gypsum. According to the Tampa Tribune, "EPA's limit for use is 10 picocuries of radium per gram, well below the levels usually found in the mounds."

A recent statement from the EPA reads:

"Only two uses (for the gypsum) are permitted: limited agricultural use and research. Other uses may be proposed, but otherwise the phosphogypsum must be returned to mines or stored in stacks."

11) Commercial Uranium Production ([back to top](#))

While the presence of uranium decay-products makes gypsum a tough sell for the phosphate industry, the uranium has, at various times, presented the industry with a business opportunity of its own.

One of the lesser-known-facts about the phosphate industry is that its processing facilities have produced and sold sizeable quantities of uranium.

In 1997, just two phosphate plants in Louisiana produced 950,000 pounds of commercial uranium, which amounted to roughly 16% of the domestically produced uranium in the US.

In 1998, the same two plants produced another 950,000 pounds, but due to declining market prices for uranium, both plants have since ceased production.

B-62

If market prices improve, however, 4 US phosphate plants (2 in Louisiana & 2 in Florida) would have the capacity to produce a combined 2.75 million pounds of uranium per year, according to the Department of Energy (DOE). The DOE has termed these 4 facilities "Nonconventional Uranium Plants."

12) Cold War Secrets & Worker Health ([back to top](#))

The Department of Energy has not always been so open about the uranium-making potential of the phosphate industry. During the Cold War, its predecessor institution, the Atomic Energy Commission (AEC), kept this fact closely under wraps - even to the workers who were, unknowingly, handling large quantities of the radioactive material.

In Joliet, Illinois, it has only recently come to light that the local phosphate plant had secretly produced some 2 million pounds of uranium for the US government in the years 1952 to 1962. According to local newspaper reports, the cancer rates of people who worked at the plant, especially "Building 55" where the uranium was processed, are unusually high.

"We used to kind of joke that if you worked for Blockson, you got cancer," quipped Vince Driscoll, the son of a cancer-stricken worker.

Today, with the Cold War over, it is becoming clear that workers in the phosphate industry need special protection. According to a report from the European Commission:

"Processing and waste handling in the phosphate industry is associated with radiation levels of concern for workers and the public. The level of protection for these groups should be more similar to the level of protection that is state of the art in other industries, particularly the nuclear industry."

13) Wastewater Issues ([back to top](#))

While the radioactivity of the gypsum stacks has probably been the key health concern of the EPA, it is not the only one.

Resting atop the phosphate industry's gypsum piles are highly-acidic wastewater ponds, littered with toxic contaminants, including fluoride, arsenic, cadmium, chromium, lead, mercury, and the various decay-products of uranium. This combination of acidity and toxins makes for a poisonous, high-volume, cocktail, which, when leaked into the environment, wreaks havoc to waterways and fish populations. As noted by the St. Petersburg Times, "Spills from these stacks have periodically poisoned the Tampa Bay environs."

One spill, in 1997, from a now-defunct gypsum stack in Florida, "killed more than a million fish."

"Strike the Alafia River off your list of fishing spots," wrote one journalist after the spill. "It's gone, dead as a sewer pipe, killed by the carelessness of yet another phosphate company."

Today, the same gypsum stack which caused this particular spill, is considered by Florida's Department of Environmental Protection to be "the most serious pollution threat in the state." That's because tropical rains over the past couple of years have brought the wastewater to the edge of the stack's walls.

As noted by the Tampa Tribune, "The gypsum mound is near capacity, and a wet spring or a tropical storm could cause a catastrophic spill."

To prevent such a spill, which was all but inevitable, the EPA recently agreed to let Florida pursue "Option Z": To load 500-600 million gallons of the wastewater onto barges and dump it directly into the Gulf of Mexico.

The dumping of the wastewater into the Gulf represents the latest in a series of high-profile embarrassments for Florida's phosphate industry; one of the most dramatic of which happened on June 15, 1994.

On that day, a massive, 15-story sinkhole appeared in the middle of an 80 million ton gypsum stack. The hole was so big that, according to US News & World Report, it

"could be as big as 2 million cubic feet, enough to swallow 400 railroad boxcars. Local wags call it Disney World's newest attraction -- 'Journey to the Center of the Earth.'"

But, as US News noted,

"there's nothing amusing about it. The cave-in dumped 4 million to 6 million cubic feet of toxic and radioactive gypsum and waste water into the Floridan aquifer, which provides 90 percent of the state's drinking water."

And so it goes.

As summarized by the Tampa Tribune:

"It's not like you can padlock the doors and walk away. The complexities of keeping a phosphate processing plant operating are becoming clear to government regulators now overseeing two of them. Ponds full of 1.5 billion gallons of acid and three mountains of radioactive waste mean you just can't shut off the machinery and turn out the lights. The state could be stuck with the plants for years. And taxpayers would be stuck with the tab."

14) REFERENCES [\(back to top\)](#)

Full citations of the studies listed above, can be accessed at:

<http://www.fluoridealert.org/phosphate/overview-refs.htm>

Note: Full-text copies of all newspaper articles cited in this article can be accessed by clicking on the links within the text.

15) PHOTOGRAPHS OF THE PHOSPHATE INDUSTRY [\(back to top\)](#)

Photographs of the phosphate industry are available at:
<http://www.fluoridealert.org/phosphate/photographs.htm>

16) FURTHER READING [\(back to top\)](#)

(Many thanks to Anita Knight for continually supplying FAN with newspaper articles on the phosphate industry in Florida.)

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February 19, 2005

B-64

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[Back to top](#)

B-6

Phosphate rich organic manure

From Wikipedia, the free encyclopedia

Phosphate rich organic manure is a type of fertilizer used as an alternative to diammonium phosphate and single super phosphate.

Phosphorus is required by all plants but is limited in soil, creating a problem in agriculture. In many areas phosphorus must be added to soil for the extensive plant growth that is required in crop production. Phosphorus was first added as a fertilizer in the form of single super phosphate (SSP) in the mid-nineteenth century, following research at Rothamsted Experimental Station in England.

The world consumes around 140 million tons of high grade rock phosphate mineral today, 90% of which goes into the production of diammonium phosphate (DAP). Excess application of chemical fertilizers in fact reduces the agricultural production as chemicals destroy natural soil flora and fauna. When DAP or SSP is applied to the soil only about 30% of the phosphorus is used by the plants, while the rest is converted to forms which cannot be used by the crops ^[x1,X2], a phenomenon which is known as phosphate problem to soil scientists.

Directly mixing finely ground rock phosphate mineral into organic manure produces a fertilizer known as **phosphate rich organic manure** (PROM). Research indicates that this substance may be a more efficient way of adding phosphorus to soil than applying chemical fertilizers.^{[1][2]} Other benefits of PROM are that it supplies phosphorus to the second crop planted in a treated area as efficiently as the first, and that it can be produced using waste solids recovered from the discharge of biogas plants.

Phosphorus in rock phosphate mineral is mostly in the form of tricalcium phosphate, which is water insoluble. Phosphorus dissolution in the soil is most favorable at a pH between 5.5 and 7.^[3] Ions of aluminum, iron, and manganese prevent phosphorus dissolution by keeping local pH below 5.5, and magnesium and calcium ions prevent the pH from dropping below 7, preventing the release of phosphorus from its stable molecule.^[3] Microorganisms produce organic acids and heat, allowing the slow dissolution of phosphorus from rock phosphate dust added to the soil, allowing more phosphorus uptake by the plant roots. Organic manure can prevent ions of other elements from locking phosphorus into insoluble forms. The phosphorus in phosphate enhanced organic manure is water insoluble, so it does not run into ground water or runoff ^[x] any more than that from chemical fertilizers.

Most phosphate rocks can be used for phosphate rich organic manure. It was previously thought that only those rocks which have citric acid soluble phosphate and those of sedimentary origin could be used.^[2] Rocks of volcanic origin can be used as long as they are ground to very fine size.

Organic manure should be properly prepared for use in agriculture, reducing the C:N ratio to 30:1 or lower. Alkaline and acidic soils require different ratios of phosphorus.

PROM is known as a green chemistry phosphatic fertilizer. Addition of natural minerals or synthetic oxides in water insoluble forms that contain micronutrients such as copper, zinc, and cobalt may improve the efficiency of PROM. Using natural sources of nitrogen, such as *Azolla*, may be more environmentally sound.^[4]

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- ↑ [1]
- ↑ *a b* [2]
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- ↑ [3]

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAR 30 1983

OFFICE OF
WATER

Leslie A. Russell, D.M.D.
363 Walnut Street
Newtonville, Mass. 02160

Dear Dr. Russell:

Thank you for your letter of March 9, 1983, in regard to the fluoridation of drinking water.

The information available to the Environmental Protection Agency is that fluoridation is a safe and effective means for reducing the occurrence of dental caries. The fluoridation process has been endorsed by several Presidents of the United States and by several Surgeons General, including the current Surgeon General, Dr. C. Everett Koop. A copy of Dr. Koop's statement on fluoridation is enclosed.

Water treatment chemicals, including fluosilicic acid, have been evaluated for their potential for contributing to the contamination of drinking water. The Water Treatment Chemicals Codex, published by the National Academy of Sciences, prescribes the purity requirements for fluosilicic acid and other fluoridation chemicals.

In regard to the use of fluosilicic acid as a source of fluoride for fluoridation, this Agency regards such use as an ideal environmental solution to a long-standing problem. By recovering by-product fluosilicic acid from fertilizer manufacturing, water and air pollution are minimized, and water utilities have a low-cost source of fluoride available to them. I hope this information adequately responds to your concern.

Sincerely yours,

Rebecca Hanmer

Rebecca Hanmer
Deputy Assistant Administrator
for Water

Enclosure

B-69

03/14/08 14:04

904 241 1220

JACKSONVILLE FL

004/004

Invoice 60147

Invoice Date 11/01/2006

Lucier Chemical Industries, Ltd.
PO Box 49000
Jacksonville Beach, FL 32250 USA

Telephone: 904/241-1200

Please remit to:

LCI, Ltd.

P.O. Box 790051

St. Louis, Mo 63179-0051

Bill To:

PORT ANGELES, CITY OF
P.O. BOX 1150
ATTN: WATER DIVISION
PORT ANGELES, WA 98362
USA

Ship To:

PORT ANGELES, CITY OF
3501 WEST 18TH STREET
FLUORIDATION PLANT
PORT ANGELES, WA 98363

Customer	Carrier	F.O.B.	Terms		
PORT05	JJ WILLIAMS	DELIVERED	Net 30 Days		
Purchase Order Number		Freight Terms	Our Order Number		
Verbal		PREPAID BY LCI	11011601		
Qty. Ordered	Qty. Shipped	Item	Contract Price	Adjusted Price	Extended Price
	Qty. Adjusted	Item Description	Discount	Tax	
12.500	11.940	HFS	530.000@ 25%	520.48000	6214.29
	11.940	Fluorosilicic Acid, 8, Lot No. G20361 Analysis: 24.550			
Ordered 25,000 #					
Nontaxable Subtotal					6214.29
Taxable Subtotal					0.00
Tax					0.00
Total Invoice					6214.29

B-70

FLUORIDE ACTION NETWORK HEALTH EFFECTS

HEALTH EFFECTS HOMEPAGE

[Accidents](#)

[Allergy](#)

[Arthritis](#)

[Bone Disease](#)

[Brain](#)

[Cancer](#)

[Dental Fluorosis](#)

[EPA Standards](#)

[Gastrointestinal](#)

[Infant Exposure](#)

[Immune System](#)

[Kidney](#)

[Pineal Gland](#)

[Respiratory](#)

[Reproductive](#)

[Thyroid Gland](#)

[Tooth Decay](#)

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[Glossary of Terms](#)

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HEALTH EFFECTS: Fluoride & the Kidneys

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Summation - Fluoride & the Kidneys: (Click for more detail)

Kidney disease markedly increases an individual's susceptibility to fluoride toxicity.

The kidneys are responsible for ridding the body of ingested fluoride, and thereby preventing the buildup of toxic levels of fluoride in the body.

In healthy adults, the kidneys are able to excrete approximately 50% of an ingested dose of fluoride.

However, in adults with kidney disease the kidneys may excrete as little as 10 to 20% of an ingested dose - thus increasing the body burden of fluoride and increasing an individual's susceptibility to fluoride poisoning (e.g. renal osteodystrophy).

The bone changes commonly found among patients with advanced kidney disease closely resemble the bone changes found among individuals with the osteomalacic-type of skeletal fluorosis. This raises the possibility that some individuals with kidney disease are suffering from undiagnosed skeletal fluorosis.

As noted by Dr. Edward Groth, a veteran Senior Scientist at Consumers Union:

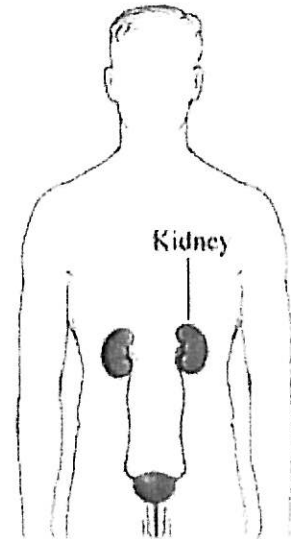
"It seems probable that some people with severe or long-term renal disease, which might not be advanced enough to require hemodialysis, can still experience reduced fluoride excretion to an extent that can lead to fluorosis, or aggravate skeletal complications associated with kidney disease... It has been estimated that one in every 25 Americans may have some form of kidney disease; it would seem imperative that the magnitude of risk to such a large sub-segment of the population be determined through extensive and careful study. To date, however, no studies of this sort have been carried out, and none is planned" (Groth 1973; Doctoral Thesis; Stanford University).

Because the kidney accumulates more fluoride than all other soft tissues (with the exception of the pineal gland), there is concern that excess fluoride exposure may contribute to kidney disease - thus initiating a "vicious cycle" where the damaged kidneys increase the accumulation of fluoride, causing in turn further damage to the kidney, bone, and other organs.

The possibility that fluoride exposure can cause direct damage to kidney tissue is supported by a long line of animal and human studies.

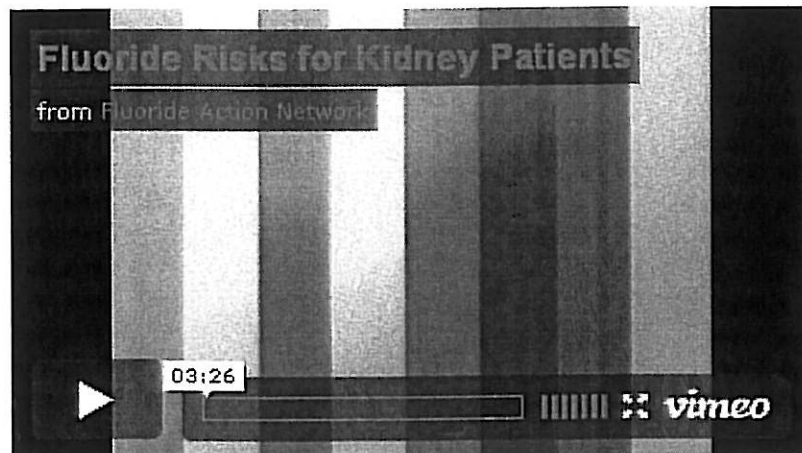
In studies on fluoride-exposed animals, kidney damage has been reported at levels as low as 1 ppm if the animals consume the water for long periods of time.

In humans, elevated rates of kidney damage are frequently encountered among populations with skeletal fluorosis. In addition, several case reports



B-71

suggest that some individuals with kidney disease can experience significant recovery in their clinical signs and symptoms following the provision of fluoride-free water.



VIDEO: Fluoride Risks for Kidney Patients (see also [YouTube version](#))

Fluoride & the Kidneys - Studies Available Online: ([back to top](#))

EXCERPT - html: Johnson W, et al. (1979). *Fluoridation and bone disease in renal patients*. In: E Johansen, DR Taves, TO Olsen, Eds. Continuing Evaluation of the Use of Fluorides. AAAS Selected Symposium. Westview Press, Boulder, Colorado. pp. 275-293.

Fluoride & the Kidneys - Articles of Interest: ([back to top](#))

- [National Kidney Foundation Admits: Kidney Patients Should be Notified of Potential Risk from Fluorides and Fluoridated Drinking Water - The Lillie Center, June 3, 2008](#)
- [Utility official sees wife's health approve since fluoride dropped - The Daily Times, Maryville, Tennessee; April 4, 2005](#)

Fluoride & the Kidneys - Kidney Patients at Increased Risk of Fluoride Poisoning: ([back to top](#))

"[A] fairly substantial body of research indicates that patients with chronic renal insufficiency are at an increased risk of chronic fluoride toxicity. Patients with reduced glomerular filtration rates have a decreased ability to excrete fluoride in the urine. These patients may develop skeletal fluorosis even at 1 ppm fluoride in the drinking water... The National Kidney Foundation in its 'Position Paper on Fluoride—1980' as well as the Kidney Health Australia express concern about fluoride retention in kidney patients. They caution physicians to monitor the fluoride intake of patients with advanced stages of kidney diseases. However, a number of reasons will account for the failure to monitor fluoride intake in patients with stages 4 and 5 of chronic kidney diseases and to detect early effects of fluoride retention on kidneys and bone. The safety margin for exposure to fluoride by renal patients is unknown, measurements of fluoride levels are not routine, the onset of skeletal fluorosis is slow and insidious, clinical symptoms of this skeletal disorder are vague, progression of renal functional decline is multifactorial and physicians are unaware of side effects of fluoride on kidneys or bone."

SOURCE: Schiff H. (2008). Fluoridation of drinking water and chronic kidney

disease: absence of evidence is not evidence of absence. Nephrology Dialysis Transplantation 23:411.

✓ "Individuals with kidney disease have decreased ability to excrete fluoride in urine and are at risk of developing fluorosis even at normal recommended limit of 0.7 to 1.2 mg/l."

SOURCE: Bansal R, Tiwari SC. (2006). Back pain in chronic renal failure. Nephrology Dialysis Transplantation 21:2331-2332.

✓ "Persons with renal failure can have a four fold increase in skeletal fluoride content, are at more risk of spontaneous bone fractures, and akin to skeletal fluorosis even at 1.0 ppm fluoride in drinking water."

SOURCE: Ayoob S, Gupta AK. (2006). Fluoride in Drinking Water: A Review on the Status and Stress Effects. Critical Reviews in Environmental Science and Technology 36:433-487

"In patients with reduced renal function, the potential for fluoride accumulation in the skeleton is increased. It has been known for many years that people with renal insufficiency have elevated plasma fluoride concentrations compared with normal healthy persons and are at a higher risk of developing skeletal fluorosis."

SOURCE: National Research Council. (2006). Fluoride in Drinking Water: A Scientific Review of EPA's Standards. National Academies Press, Washington D.C. p140 .

"Skeletal fluorosis seems possible, especially in hot climates or with renal compromise, from drinking excessive quantities of instant or bottled teas. Our observations support the need for better understanding of the amounts and systemic effects of fluoride in teas."

SOURCE: Whyte M. (2006). Fluoride levels in bottled teas. American Journal of Medicine 119:189-190.

"We hypothesize that elevated serum F levels might contribute to the disturbances in mineral ion homeostasis that are observed in patients with CRI [Chronic Renal Insufficiency]. This is of particular concern since the incidence of dental fluorosis has increased due to increased F- uptake from multiple fluoridated sources. The ubiquitous presence of F in food and beverage products regardless of the degree of water fluoridation suggests that the overall F exposure in individuals with CRI may need to be more closely monitored."

SOURCE: Mathias RS, et al. (2000). Increased fluoride content in the femur growth plate and cortical bone of uremic rats. Pediatric Nephrology 14:935-939

"It is important to control the intake of this element [fluoride] and the prolonged use of fluoridated dental products in the subjects with chronic renal insufficiency, to avoid a risk of fluorosis."

SOURCE: Torra M, et al. (1998). Serum and urine fluoride concentration: relationships to age, sex and renal function in a non-fluoridated population. Science of the Total Environment 220: 81-5.

"[A] fairly substantial body of research indicates that people with kidney dysfunction are at increased risk of developing some degree of skeletal fluorosis. ... However, there has been no systematic survey of people with impaired kidney function to determine how many actually suffer a degree of skeletal fluorosis that is clearly detrimental to their health."

SOURCE: Hileman B. (1988). Fluoridation of water. Questions about health risks and benefits remain after more than 40 years. Chemical and Engineering News August 1, 1988, 26-42.

"It seems probable that some people with severe or long-term renal disease, which might not be advanced enough to require hemodialysis, can still experience reduced fluoride excretion to an extent that can lead to fluorosis, or aggravate skeletal complications associated with kidney disease... It has been estimated that one in every 25 Americans may have some form of kidney disease; it would seem imperative that the magnitude of risk to such a large