

**REPORT OF THE
FORT COLLINS
FLUORIDE TECHNICAL
STUDY GROUP**

April 2003

The following agencies collaborated on the Fort Collins Fluoride Technical Study Group Process:

- Fort Collins Utility Department
- Health District of Northern Larimer County
- Larimer County Board of Health

In addition to the Fluoride Technical Study Group, the following people assisted in the development of these findings:

- Fluoride Technical Study Group Research and Administrative Support
Susan Hewitt
Health District of Northern Larimer County
Fort Collins, Colorado
- Public Involvement Support
Patty Bigner
City of Fort Collins, Colorado
- Facilitation
Mike Hughes
RESOLVE
Denver, Colorado

Table of Contents

Table of Contents	i
Executive Summary	iii
Introduction	1
Finding #1 – The Effectiveness of Drinking Water Fluoridation in Preventing Caries	9
Historical Perspective	9
How Fluoride Works	13
Evidence of Effectiveness of Community Water Fluoridation	14
Evidence of the Current Magnitude of Effectiveness	16
Studies of the Effectiveness of Community Water Fluoridation in Adults	18
Fluoridation-Ended Sites in Which No Caries Increases Were Found	18
Gaps in Knowledge.....	20
FINDINGS: The Effectiveness of Drinking Water Fluoridation in Preventing Caries (Cavities)	21
Reference List	22
Finding #2 – The Risk of Drinking Water Fluoridation	25
Total Exposure to Fluoride	25
FINDINGS: Total Fluoride Exposure	30
Review of Potential Adverse Health Effects	30
Cancer	30
FINDINGS: Cancer	34
Bone Fractures and Osteoporosis	34
FINDINGS: Bone Effects	37
Skeletal Fluorosis.....	37
FINDINGS: Skeletal Fluorosis	40
Dental Enamel Fluorosis.....	40
FINDINGS: Dental Fluorosis	44
Thyroid Function	44
FINDINGS: Thyroid Function	45
Immune System Effects	45
FINDINGS: Immunological Effects	46
Other Potential Health Effects	46
FINDINGS: Other Health Effects	48
Reference List	49
Finding #3 – Costs and Benefits, Including the Distribution of Costs and Benefits	51
Cost-Effectiveness of Community Water Fluoridation	51
Distributional Effects of Community Water Fluoridation	55
Effectiveness and Cost-Effectiveness of Other Fluoride Modalities Relative to Community Water Fluoridation	56
FINDINGS: Costs and Benefits	58
Reference List	59
Finding #4 – The Potential for Increased Contaminant Levels Due to the Use of Hydrofluorosilicic Acid	61
Background.....	61
Fluoride Sources	61
Fluoride Manufacturing Process	61
Methods of Application	61

Water Quality	63
Analytical Information	63
Uncertainties	66
FINDINGS: The Potential for Increased Contaminant Levels Due to the Use of Hydrofluorosilicic Acid	71
Reference List	72
Appendix A-1 – Fort Collins Fluoride Technical Study Group Tiered Reference List	73
First Tier	73
Other Literature Reviewed	74
Materials Submitted by Members of the Public	95
Appendix A-2 – Fluoride Mass Balance Calculations City of Fort Collins Water Treatment Facility	101
Appendix 1 – Effectiveness of Community Water Fluoridation Methodological Approaches of “Tier One” and Other Reviews	103
Tier 1 Reviews	103
Other Reviews	106
Appendix 2 – Risks According to “Tier One” Reviews	109
Introduction	109
Cancer	110
Bone Fractures and Other Bone Effects	119
Skeletal Fluorosis	127
Enamel (Dental) Fluorosis	133
Other Health Effects	144
Appendix 3 – Cost Effectiveness Studies	159
Table 1: Cost-Effectiveness Studies, U.S.	159
Table 2: Cost-Effectiveness Studies, Other Countries	163
Table 3: Other Delivery Strategies for Fluoride	167
Table 4: Other Strategies for Primary Prevention of Dental Caries	170
Economic Analysis of Community Water Fluoridation in Fort Collins, Colorado	172
References	174
Appendix 4 – The Potential for Increased Contaminant Levels Due to the Use of Hydrofluorosilicic Acid	175
4.1 Material Safety Data Sheet Fluoride	175
4.2 Fluoride Manufacturing Process, Figures 1 and 2	181
4.3 Report Form 1	183
4.4 NSF Certification	184
4.5 Fort Collins Utilities Drinking Water Consumer Confidence Report, 2001	188
4.6 Fort Collins Utilities Drinking Water Quality Summary, 2001 and 2002	190
4.7 Results for Iron, Copper, Manganese, Zinc, Cadmium and Nickel, Figures 3 – 9	193
4.8 Arsenic Concentration in Finished Water	194
4.9 Peer Reviews of the Masters and Coplan Report	198
4.10 Lead Data Regression Analysis	225

Introduction

In response to questions from the public about the risks, benefits and costs of community drinking water fluoridation, the City of Fort Collins convened the Fluoride Technical Study Group (FTSG) to fulfill the following responsibility:

- To explore information related to the costs and benefits of community drinking-water fluoridation;
- To summarize what is known and not known about the risks and benefits of adding fluoride;
- To summarize what is known and not known about the risks and benefits of not adding fluoride;
- To develop and present findings;
- To base findings on the high quality scientific and technical information;
- To work toward consensus findings whenever possible;
- To clarify areas of agreement and of disagreement about the implications of the information;
- To integrate public input into the recommendations; and
- To present data, consensus findings and areas of disagreement to the Board of Health and the Water Board so that these two boards can offer informed recommendations to the Fort Collins City Council.

The Fluoride Technical Study Group (FTSG) includes nine community members with an interest in the questions surrounding community drinking water fluoridation and with specific technical, medical or scientific capabilities. The FTSG members are:

Ed Carr, DC, MS
Chiropractor and Wellness Counselor

Bruce Cooper, MD, MSPH
Medical Director
Health District of Northern Larimer County

Greg Evans, DDS
Pediatric Dentist

Kevin Gertig
Certified Colorado Water Works
Operator A
Water Production Manager
Fort Collins Utilities Water Treatment Plant

Adrienne LeBailly, MD, MPH *
Director, Larimer County
Department of Health and Environment

Gale McGaha Miller, BS
Water Quality Services Manager
Fort Collins Utilities

Rami Naddy, PhD
Environmental Toxicologist
ENSR International
Member of City of Fort Collins
Water Board

John Reif, DVM, MSc (Med)
Professor
Department of Environmental Health
Colorado State University

Frank Vertucci, PhD, MS
Certified Senior Ecologist
ENSR International
Vice President of the
Larimer County Board of Health

* Although Dr. LeBailly's workload necessitated that she withdraw from the review process in Summer 2002, she was very active in early meetings and helped establish guidelines and review criteria. She has continued to follow the group's proceedings.

Process

The Fluoride Technical Study Group (FTSG) met monthly as a full group, once each month, between December 2001 and November 2002. During the report drafting process in the latter half of 2002, smaller subsets of FTSG members met frequently to draft various sections of this document. The FTSG met three times in December of 2002 to reach final consensus on the document. In addition, the FTSG held two public meetings in early 2002 to invite input and advice from the public before beginning its work, and two in early 2003 to present and discuss report findings.

Throughout the process, the FTSG encouraged ongoing public input. Of particular note is the fact that at least one-third of the FTSG members examined every technical study, journal article, newspaper article or videotape submitted by members of the public. All nine members reviewed those public submissions deemed by any one member to be of significant scientific or technical merit, and therefore worthy of inclusion in the FTSG deliberations. The technical and scientific information was assembled, reviewed and distributed to the FTSG by Susan Hewitt of the Health District of Northern Larimer County, who also assisted in editing and preparing the final draft report.

The FTSG also made efforts to keep the public informed of the work that was being accomplished. All FTSG meetings were open to the public, although no public comment was taken at these meetings. Summaries of the public meetings and the FTSG meetings were posted on a website maintained by the Fort Collins City Utility Department. Additionally, three sets of the reference materials used by the FTSG were available for review by members of the public at three locations in Fort Collins.

Priorities

In its earliest meetings (and after public meetings that elicited important topics) the FTSG prioritized the key questions and centered its inquiry on developing findings in response to these priorities. The FTSG reviewed the scientific and technical literature for information about seven topics, six broad topics and one specific to a single disease end point:

- The effectiveness of drinking water fluoridation
- The risk of drinking water fluoridation
- The risk of cumulative exposure to fluoride (over time) from all sources, including drinking water,
- The costs and benefits of not fluoridating the drinking water supply, including assessing the distribution costs and benefits (equity)
- The effectiveness of alternative methods of delivering fluoride
- The effectiveness of addressing fluoridation as a public health issue and the effectiveness of addressing fluoridation as an individual choice
- The risk of impacts to thyroid function due to drinking water fluoridation

After generating its initial draft of this report, the FTSG has consolidated its findings into these four topics:

1. The effectiveness of drinking water fluoridation.
2. The risks of drinking water fluoridation and of cumulative exposure to fluoride from all sources, including drinking water, over time (with specific attention to cancer, bone fractures, skeletal fluorosis, dental fluorosis and thyroid function).
3. The costs and benefits of fluoridating the drinking water supply, and of not fluoridating the drinking water supply, including assessing the distribution costs and benefits (equity), and including the costs and benefits of using alternative methods to deliver fluoride.
4. The potential for increased contaminant levels in the drinking water due to the use of hydrofluorosilicic acid in the fluoridation process.

Technical Study Group Literature Review Method

From the start, it was acknowledged that the published scientific literature base on community water fluoridation was enormous and that it was beyond the scope of this group to conduct a systematic review of thousands of primary studies. The FTSG elected to use a tiered approach to reviewing the existing literature on water fluoridation, turning first to already conducted and published scientific literature research reviews and compilations. Only when a gap in the data became evident or when a specific need for more information was needed did the group turn to and evaluate published, peer-reviewed primary studies. Initially, a half dozen comprehensive literature reviews were located and shared by the FTSG, with additional studies and compilations located during the process. Ultimately, a tiered arrangement of the literature utilized by the FTSG was compiled.

- “Tier One” literature were those by well-known, authoritative and unbiased national and international public health agencies such as the United States Public Health Service, the World Health Organization, the United States Centers for Disease Control and Prevention, the National Institutes of Health, the Medical Research Council of Great Britain, and the British National Health Services Centre for Reviews and Dissemination.
- The next tier included:
 - Published literature reviews and meta-analyses.
 - Reports of primary studies published in peer-reviewed journals that were used to fill data gaps or when additional explanation was needed.
 - Literature reviews conducted by or contracted by municipal, provincial, or other local governmental entities that were used for local decision making. These were primarily used to identify “Tier One” studies and primary literature.
- Other materials considered by the FTSG included editorials, commentary and fact sheets, some of which were supplied by members of the public.

Concerning “Tier One” and other literature, each of these studies used different search and review strategies. Some used explicitly stated and highly systematic methods to evaluate the scientific merit of studies, while others used more implicit and more subjective methods such as relying on an evaluation of the quality of the literature by subject matter experts. The tiered reference list is provided in Appendix A-1. Additional information on the search and review strategies of many of the tier one literature and other documents is presented in Appendix 1.

Study Criteria

The FTSG, for the most part, limited consideration to scientific studies of drinking water fluoridation at or around 1 milligram per liter (mg/L) or 1 part per million (ppm), because it is the target amount of fluoride added to the Fort Collins city water supply (range of 0.7 – 1.2 mg/L with data indicating stringent control at 1.0 mg/L). In some cases, studies where experimental animals were dosed at a higher level or human epidemiological or pharmacological studies of populations exposed to higher doses of fluoride were considered by the FTSG to better understand potential cumulative or dose-dependent effects.

Please note the terms part per million (ppm) and milligrams per liter (mg/L) are used interchangeably throughout this report. They are more or less equivalent and each term is used by the literature cited by the FTSG. In layman’s terms 1 ppm or 1 mg/L fluoride represents one “drop” of fluoride in one million “drops” of water.

Weight of Evidence Approach With Uncertainties

Members of the FTSG used the weight of evidence approach in evaluating scientific studies. The EPA defines the weight of evidence approach as “Considerations in assessing the interpretation of published information about toxicity—quality of testing methods, size and power of study design, consistency of results across studies, and biological plausibility of exposure-response relationships and statistical

associations” (<http://www.epa.gov/OCEPATERMS/>). Thus, all the scientific literature on a topic is evaluated, with studies categorized into levels of better and lesser studies based on such variables as degree of measurement accuracy, number of study subjects, how data was collected, control of potential confounding factors and so on. The best studies get the most weight and the poorer studies less weight or disqualification if a certain standard is not met. Particular attention is given when multiple studies, by different researchers, using different methods, in varied population groups reach similar conclusions. Such findings generally corroborate hypotheses and are particularly useful when looking for subtle health changes due to the large numbers of subjects measured. The converse is also important, if multiple studies show contradictory positive or negative effects then no overall effect is discernable and hypotheses may be refuted before a link is made to potential harm or benefit. The FTSG acknowledged uncertainties are inherent when scientific literature is evaluated.

Some members advocated for the precautionary principle, defined by the EPA as “When information about potential risks is incomplete, basing decisions about the best ways to manage or reduce risks on a preference for avoiding unnecessary health risks instead of on unnecessary economic expenditures” (<http://www.epa.gov/OCEPATERMS/>). In other words, to assist the risk managers, the weight of evidence is considered as well as the magnitude of the calamity that a worst-case scenario may produce if the evidence is flawed or inaccurate.

The FTSG endeavored to create a balanced report for use by decision-makers that took into account the most current and best available analysis of the weight of the scientific evidence on the risks and benefits of community water fluoridation. The group also acknowledged that there are gaps in the knowledge and uncertainties are inherent in the ability to fully understand what may be subtle, yet important health effects that are yet to be detected via a weight of the evidence approach. Thus, the report includes stated uncertainties and areas where additional research is needed to better understand the true benefits and risks.

Strengths and Limitations of Epidemiology and Toxicology Approaches

The potential risks of exposure to fluoride among human populations can be evaluated in essentially two ways. In the first approach, laboratory animals are tested under controlled conditions and exposed to known quantities of fluoride in water or food for varying lengths of time. Toxicological studies attempt to derive dose-response relationships between exposure to fluoride and some measure of organismal response. Measured responses may include mortality, changes in growth, reproductive capacity or the incidence of cancerous lesions. In some studies, rodents are exposed over their entire lifetime, up to two years. These studies typically include histologic examination of tissues at the end of the study to detect microscopic lesions in multiple organs. Doses of fluoride given to animals are often much higher than doses that would typically be encountered by a person.

Extrapolation of dose-response toxicity tests in animals to the prediction of human risks from drinking water exposure to fluoride is complicated by many factors. Findings must be extrapolated between the differences in doses used in animal studies and the range of human exposures associated with the consumption of 1mg/l (1ppm) of fluoride in fluoridated drinking water. Animal responses can vary compared to human responses, and there is always uncertainty associated with extrapolation from test species like rodents to humans. Absence of a dose-response relationship between a stressor and a response is considered strong evidence that the stressor is not likely to cause a response. However, the absence of any observed dose-response relationship between a stressor and a response does not prove that the stressor cannot cause a response.

The second approach to assessing risk to humans incorporates epidemiologic studies of human populations. These studies involve comparing the incidence of various potential health effects among populations exposed or not exposed to fluoride or comparing the frequency of exposure to fluoride among persons with and without a certain disease. The advantages of the epidemiologic approach are that they

are conducted in the species of interest (humans), the exposures are at relevant levels and the study is done by observational, rather than experimental methods under “natural” conditions.

The disadvantages of epidemiologic approaches are that they may make it difficult to accurately assess exposure over time due to lack of individual level data about diet, water consumption patterns, fluoride concentrations, etc. These studies are also subject to a variety of biases found in observational research. Principal sources of bias in epidemiologic studies include 1) confounding - where there may be exposure to another variable that may be more common among those exposed that is also a risk factor for the disease, resulting in an over- or under-estimate of the true risk; 2) selection bias due to an inability to study entire populations, resulting in a biased sample of participants whose exposures or disease patterns are not representative of the population from which they are drawn; and 3) information bias, where information about exposures, outcomes or other factors may be inaccurate due to problems with recall, residential mobility, lack of adequate exposure data and other data inadequacies.

The FTSG reviewed the toxicological and epidemiological studies as independent lines of evidence. The weight of evidence findings are stronger when the toxicological and epidemiological studies agree. However, either line of evidence may carry enough weight on its own to be convincing as to the benefits or risks of a particular substance. In one example, the EPA’s recent ruling to lower the maximum contaminant level for arsenic in drinking water from 50 µg/liter to 10 µg/liter came solely from epidemiologic studies indicating an increased risk of cancer in exposed human populations. Also in the cancer arena, toxicological evidence may stand alone if a substance is tested repeatedly in several experimental test species (such as rats, mice, and hamsters) at suitable doses, and a specific cancer is detected consistently in a sufficient proportion of test animals. The toxicological evidence is much stronger when the same substance is also shown, in a variety of genetic test systems, to have DNA-damaging effects (genotoxicity) that have been associated with cancer in humans.

Risk and Benefit Assessment and Risk Management

The charge of the FTSG was to compile a report that assessed risks and benefits of community water fluoridation in order to assist the risk managers (i.e., the Larimer County Board of Health, the City of Fort Collins Water Board, and the Fort Collins City Council). The FTSG found the following explanation of risk management by the Medical Research Council of Great Britain to be particularly useful:

“Once the risks and benefits have been assessed, this information must be set alongside other considerations, such as the financial cost of the policy or action, and a decision then made on whether to implement the change. This is not simply a matter of science – it involves value judgments, and individuals may weight the risks, benefits and attendant uncertainties differently. If the decision must be taken at the community level (as with water fluoridation), it often falls to democratically elected representatives and may follow wider public consultation and debate” Reference cited: Medical Research Council (2002) Working Group Report: Water Fluoridation and Health. London, U.K.: John Wright, p. 7.

Statutory Authority for Fluoride Used in Community Water Fluoridation

The United States Environmental Protection Agency (EPA), under the Safe Drinking Water Act (42 USC 300), promulgates the National Primary Drinking Water Regulations. These regulations set the maximum contaminant levels (MCLs) for chemicals in finished water supplied by public water systems. Based on a report by the National Research Council, the EPA has established an MCL for fluoride of 4.0 mg/L. The National Sanitation Foundation (NSF) certifies drinking water additives if they are shown to contribute less than 10% of the MCL to the finished water supply for all drinking water contaminants regulated by the EPA. As stated above, the level of fluoride in Fort Collins treated water supplies is stringently controlled at 1.0 ppm (range from 0.7 to 1.2 ppm). The Fort Collins Utilities Water Treatment Program

complies with all regulations set forth by the EPA for fluoride, uses products that are certified by the NSF, and meets or exceeds all recommendations set forth by the Colorado Department of Public Health and Environment (CDPHE) as well as by the United States Centers for Disease Control and Prevention (CDC).

Several individuals at the initial public meetings suggested that fluoride should be treated as a drug that is added to community water and wondered why the United States Food and Drug Administration (FDA) does not regulate fluoride in drinking water. The FTSG noted that FDA considers the intended use of products when determining whether or not an “article” is a drug, as opposed to a cosmetic, a food or beverage, or none of these. The intended use of the high concentrations of fluoride in toothpaste and other dental products meets the FDA’s definition of a drug, i.e., drugs are “(A) articles intended for use in the diagnosis, cure, mitigation, treatment, or prevention of disease and (B) articles (other than food) intended to affect the structure or any function of the body of man or other animals” [FD&C Act, sec. 201(g)(1)]. Consistent with this definition, when fluoride is added to bottled water, the FDA regulates the product as a food, because of its intended use. The EPA, rather than the FDA, has the authority in the U.S. to regulate maximum levels of fluoride in drinking water. In addition, the U.S. Public Health Service and state public health authorities are charged with issuing recommendations regarding optimal levels of water fluoridation for purposes of preventing caries, and the decision to fluoridate water is left to the impacted population’s elected officials. The FTSG did not address questions of legal definitions or the distribution of regulatory authority in investigating the four outlined objectives as previously stated.

Important Background Information Relevant to the Fluoridation of Community Water in Fort Collins Colorado

History of Fort Collins Water Fluoridation Program

In 1954, an ordinance to fluoridate was presented to Fort Collins voters, but did not receive sufficient votes to pass. In 1966, the Fort Collins City Council adopted an ordinance prohibiting fluoridation unless approved by a vote of the public. Citizens voted in 1967 to authorize City Council to add fluoride to Fort Collins water supply system. That year Fort Collins began adding dry sodium silicofluoride to the treated drinking water supply at Water Treatment Plant #1. In 1992, the City changed to a liquid form of fluoride called hydrofluorosilicic acid (H_2SiF_6). This practice continues to the present.

Natural or Background Levels of Fluoride

The FTSG felt it was important for the decision-makers and the general public to know that the source waters used by the City of Fort Collins (Cache La Poudre River and Horsetooth Reservoir) contain some natural amounts of fluoride. The levels in untreated water range from 0.15 - 0.25 mg/L fluoride ion. This is below the level considered by public health authorities to be “optimal” for caries prevention. Natural fluoride is not removed during the water treatment process. If the City were to end its water fluoridation program, the drinking water in Fort Collins would continue to contain some fluoride.

Fort Collins Area Water Providers

In addition to Fort Collins Utilities, there are three additional water utilities serving the Fort Collins area (East Larimer County Water District, Fort Collins-Loveland Water District and North Weld County Water District). Currently, Fort Collins Utilities and these districts fluoridate at 1 mg/L. Neighboring districts sometimes share water. If Fort Collins Utilities ceased to fluoridate the water and some or all of the other districts continued to do so, some customers served by Fort Collins Utilities would receive fluoride in the drinking water ranging from 0.2 to 1.0 mg/L. Customers would need to contact their supplier to determine the level of fluoride in their water.

Review of Water Treatment Process Chemistry

Fort Collins Utilities uses what is termed ‘Conventional Treatment’ for its two raw water sources. Cache La Poudre River and Horsetooth Reservoir waters are blended and then treated using several different

chemicals. Each added treatment chemical is defined below and shown, beginning from left to right, on Figure 1

The water treatment chemicals used at the Fort Collins Water Treatment Facility are purchased or prepared in highly concentrated forms. Many of these concentrated chemicals are hazardous prior to their addition to the raw (untreated) water. However, once added to the raw water, these chemicals are diluted and become harmless, if not helpful. A fundamental concept in toxicology that addresses this phenomenon was first described in the sixteenth century by Paracelsus, “All substances are poisons; there is none which is not a poison. The right dose differentiates a poison from a remedy.”

Thus, any review of the “safety” of drinking water additives must keep in mind that the dose determines whether the additive is helpful or poisonous.

The reader should refer to Figure 1 to review where each of the chemicals described below are added in the treatment process.

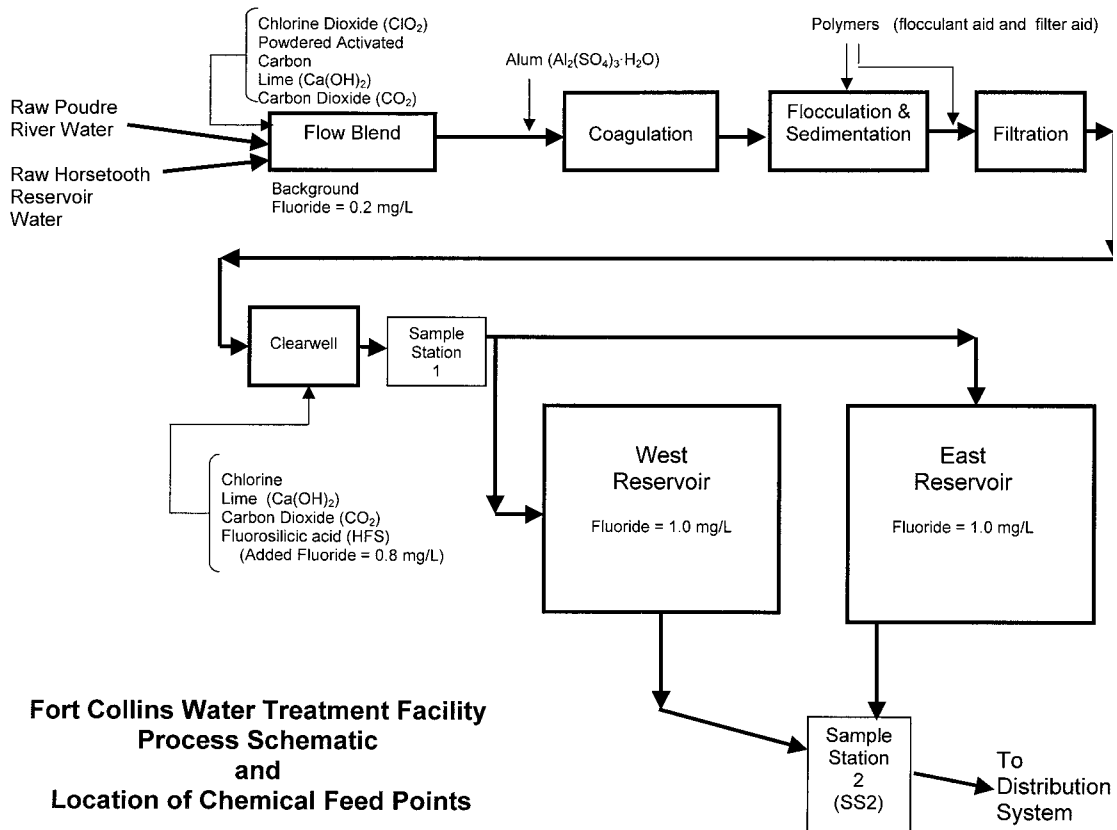


Figure 1

Chlorine Dioxide (ClO₂) - used as a pre-oxidant for Horsetooth Reservoir raw water to aid in the removal of certain contaminants. ClO₂ is made on site using a highly automated process. Chlorine, sodium chlorite, and water are blended to form chlorine dioxide solution. The solution varies in strength and dosage based on raw water quality. ClO₂ is a strong oxidant and requires special handling and feed equipment. ClO₂ disassociates to chlorite and chlorate ions as well as chlorine and hydrogen ions.

Powdered Activated Carbon (PAC) – PAC is used for removing compounds that cause taste and odor. PAC is added at dosages dependant upon raw water quality conditions. Carbon does not change chemical form after addition and is settled out of the process after addition.

Calcium Hydroxide or Lime [$\text{Ca}(\text{OH})_2$] – Lime is added to the raw water to adjust the alkalinity of the raw water prior to coagulation. Alkalinity is a measure of the buffering capacity of the water and is typically expressed as mg/l of calcium carbonate (CaCO_3). When lime is added to water, calcium ions are released and the alkalinity and pH go up (due to the increase in OH^- that is released from the lime). Dosages vary from 5 – 35 mg/L. Lime is very basic ($\text{pH} = > 10.5$).

Carbon Dioxide (CO_2) – CO_2 gas is used to adjust the pH of the raw water after lime addition (see Lime). CO_2 forms a weak acid when added to water - carbonic acid (H_2CO_3).

Aluminum Sulfate or Alum ($\text{Al}_2(\text{SO}_4)_3 + 14\text{H}_2\text{O}$) – Alum is added to the water to coagulate the particles that are present in raw, untreated water. Since alum is positively charged, and most particles are negatively charged, the particles agglomerate in the flocculation stage, and settle out in the unit process called sedimentation. Alum is slightly acidic (pH of 1 % solution = 3.5). When alum is added to water, the salts dissociate to their respective trivalent ions, Al^{+++} and then form hydroxyl complexes $\{\text{Al}(\text{H}_2\text{O})_6^{+3}\}$.

Polymers (Cationic and Anionic)- Polymers are added to the process to aid in settling the larger particles that are formed in the coagulation and flocculation processes. Different types of polymers are utilized depending on the raw water source and quality. Dosages are applied at very low concentrations (0.01 – 0.2 mg/L). Since polymers are long chained organic compounds, they do not change form and are removed with the particles that are settled and filtered out of the water.

Chlorine (Cl_2) - Chlorine is added to disinfect the water after filtration. Although chlorine is hazardous as a gas form, when added to water, Cl_2 disassociates to hypochlorous acid (HOCl) and hydrochloric acid (HCl). The HOCl is the form that disinfects the water. Dosages applied are dependant upon many water quality factors, however regulations require that a minimum of 0.2 mg/L Cl_2 remain in the water at the furthest end of the piping system that delivers water throughout our community.

Lime – Lime is also added at the clearwell to adjust the alkalinity of the finished, potable water (38 – 40 mg/L as CaCO_3). Alkalinity is a measure of the buffering capacity and is typically expressed as mg/L as calcium carbonate (CaCO_3). Again, when lime is added to the water, calcium ions are released and the pH goes up (due to the increase in OH^- that is released from the lime).

Carbon Dioxide – See above. CO_2 is used to adjust the pH of the finished, potable water. CO_2 forms a weak acid when added to water - carbonic acid (H_2CO_3). The final pH target for our community is strictly controlled (pH 7.8 – 8.0 units).

Fluorosilicic Acid (HFS or H_2SiF_6) – Fluoride is added as a liquid with very precise metering and flow measurement equipment. Liquid HFS is acidic and once added to water, it dissociates and will lower the pH of the solution. In Fort Collins, both lime and carbon dioxide are added to maintain strict pH targets of the finished water (see Figure 2).

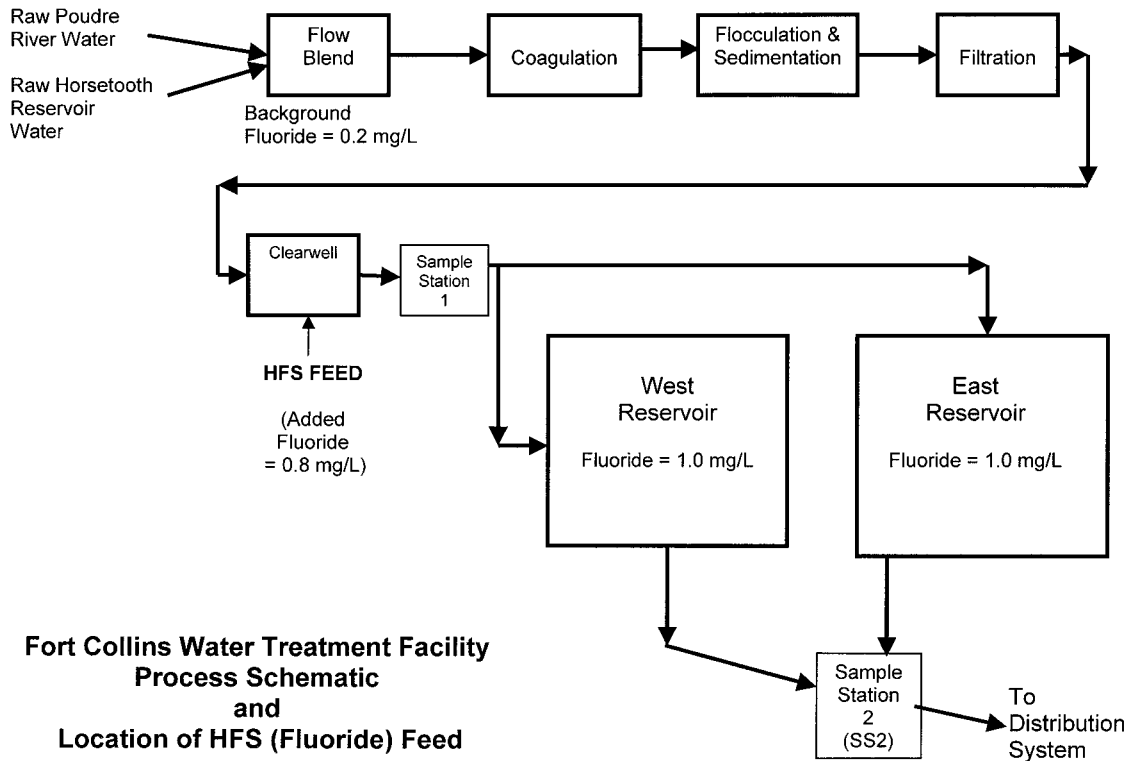


Figure 2

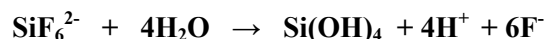
When HFS is added to water, hydrofluoric acid (HF) and silicon tetrafluoride (SiF₄) are formed. Silica tetrafluoride is a gas that reacts quickly with water to form silicic acid (H₂SiO₃) or silica (SiO₂) and HF. The HF further dissociates to hydrogen and fluoride ion. The concentration of fluoride is strictly controlled to a target level of 1 mg/L as fluoride ion.

Overview of Fluoridation Chemistry

An overview of the chemistry of HFS addition and what happens when it is dissolved in water is provided. Another overview, written by an independent research group commissioned by the British Fluoridation Society can be found at: <http://www.liv.ac.uk/bfs/wrcreport.pdf>. For detailed recent scientific reviews of this issue, the reader should consult Urbansky and Shock, 2000 and Urbansky, 2002.

Equilibrium

The equilibrium reaction between the strong acid hexafluorsilicic acid (HFS) and water can be represented in chemical shorthand as:



The dissociation of hexafluorsilicate ion (SiF₆²⁻) to the products on the right hand side of the above equation is considered to be complete at equilibrium at the normal pH of municipal water supplies (pH > 7.0). In Fort Collins, the pH is strictly maintained at a range of 7.8 – 8.0 pH units. Complete dissociation at equilibrium means chemists would report, based on the most conservative (smallest) equilibrium constants in the chemical literature, that the ratio of SiOH₄/SiF₆²⁻ at pH 8 and a F⁻ concentration of 1 mg/L would be about 1 x 10^{26.07}. That means that for every 1 molecule on non-dissociated SiF₆²⁻ there are 10,000,000,000,000,000,000,000,000 molecules of Si(OH)₄. The resulting concentration of SiF₆²⁻ at equilibrium in drinking water supplies where F⁻ is adjusted with HFS to be 1 mg/L would be exceedingly small (<<<< 1 part per trillion).

The time to achieve this equilibrium is not precisely known. However, it is known to occur within in seconds, if not minutes, in complex aqueous chemistry. Since it takes more than six hours for treated drinking water to reach Fort Collins homes, there is more than ample time for SiF_6^{2-} to reach equilibrium (i.e., to essentially fully dissociate) before any resident ingests the treated water.

Further validation of the dissociation of HFS to F^- during Fort Collins water treatment comes from the chemical mass balance calculations between the known amount of added HFS and the resulting measured F^- ion concentration presented in Appendix A-2. If large amounts of HFS were not dissociated it would be observed in the mass balance of HFS dosage versus the resulting F^- ion concentration.

It is important to put the mass balance findings into the context that no more than 66% dissociation was determined by the Westendorf, 1975 thesis cited by Masters et al 2000 (See Finding #4). This thesis finding is the “experimental evidence” cited to call into question the literature dissociation constants suggesting nearly 100% dissociation reported by Urbansky and Schock 2000, and Urbansky 2002. Since the mass balance using the F^- ion electrode method (ISE) is balanced within 3% (Mass Balance Calculations, Appendix A-2), the Fort Collins Water Treatment Facility (FCWTF) monitoring data does not support the claim that 33% or more of the HFS added is undissociated and remains in the water supply for Fort Collins. The mass balance reported an error of 3% and hence the analytical result demonstrates the dissociation of the F^- ion. Given the precision in the values used for flow rate, applied dosage rate, HFS added in pounds per day, and the F^- ion concentration, the budget +/- 3 % is within measurement error. The FCWTF data are consistent with the prediction of complete dissociation of HSF based on chemical equilibrium theory.