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Fate of Fluorosilicate Drinking Water Additives

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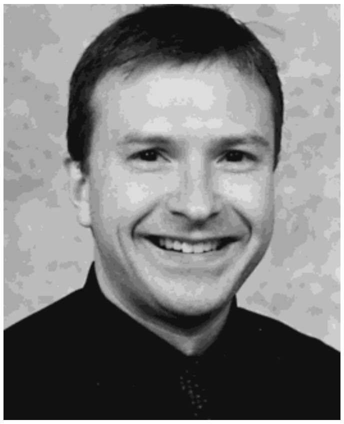
I. Introduction

A. Reasons for Renewed Interest

Periodically the EPA reexamines its information on regulated drinking water contaminants to determine if further study is required. Fluoride is one such contaminant undergoing review. The chemical literature indicates that some deficiencies exist in our understanding of the speciation of fluoride derived from fluorosilicate additives used to treat drinking water; hexafluorosilicic acid is the most commonly used additive. In addition, legislation governing the use of fluoridating agents has been proposed recently at the state level. One such bill under consideration includes language that specifically addresses issues such as partial dissociation products, products formed by reactions with other dissolved matter, and total release of F^-, and it imposes requirements that any such species be measurable at concentrations as low as 1 ng mL^{-1} in potable water.[1] Consequently, there is renewed interest in the chemistry of fluoridation processes and additives.[2] The principal objectives of this review are as follows: (1) to enumerate *unresolved chemical issues* germane to understanding fluoridation and ascertaining the fate of fluoride and fluorospecies, (2) to critically review what is known or reported, and (3) to assemble a knowledge base to provide a starting point for future study.



Ed Urbansky joined the Water Supply and Water Resources Division of the EPA's National Risk Management Research Laboratory in July 1997. Although he is an inorganic chemist, much of his work at the EPA has dealt with disinfection byproduct measurement in chlorinated or ozonated drinking water. He has also been involved in work on the perchlorate anion as an environmental contaminant. Author or coauthor of 35 peer-reviewed publications and editor of a book, *Perchlorate in the Environment*, he also serves on the Editorial Board of the *Journal of Environmental Management* and the Advisory Board of the *Journal of Environmental Monitoring*. He attended Allegheny College and Purdue University.

B. Background: Perceptions and Simplifications

A number of misconceptions and oversimplifications frequently appear in the literature, and the discussion below is intended to address them. Some of the issues are the result of recent studies, laws, or regulations, but some basic issues resurface from time to time. In 1957, a paper called “The state of fluoride in drinking water” was published, addressing many of these cyclical issues.[3] Since that time, more experimental work has been done and the knowledge base is larger, but the message is apparently being lost as many of the key outcomes have not changed. Key points may be grouped into the following categories: drinking water regulation, standards for drinking water additives, fluoridation advocacy/requirement, available fluoridation additives, testing,

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and the definition of *complete* and *fast* reaction. An overview of these issues is helpful for any researcher undertaking study of fluorosilicates as there is a wealth of misinformation available.

1. Drinking Water Regulations and Health

In the United States, federal agencies derive their respective authorities from acts of Congress and are restricted as well as empowered by those laws. Under the Safe Drinking Water Act (42 USC 300) and the amendments thereto, the EPA promulgates National Primary Drinking Water Regulations (NPDWRs) that set maximum contaminant levels (MCLs) which limit the concentration of individual species (or aggregates of species) in finished water supplied by public water systems (PWSs). On the basis of a report by the National Research Council,[4] the EPA has established an MCL of 4 mg L^{-1} (= 212 μM) for fluoride. In the United States bottled water falls under the jurisdiction of the Food and Drug Administration (FDA), and the Secretary of Health and Human Services is required to promulgate a similar rule for bottled water corresponding to every EPA drinking water regulation or to explain why no rule is needed (21 USC 349).

In 1955, Zipkin and McClure at the U.S. Public Health Service investigated several compounds for their ability to produce free fluoride available for uptake by tooth enamel, including sodium fluoride and sodium hexafluorosilicate, giving rats drinking water containing up to 50 μg mL^{-1} (as fluoride) of each.[5] Their principal motivation was to find a cheaper additive than NaF for those water utilities that opted to fluoridate. This was not a toxicological test per se. In 1962, the National Institute of Dental Research of the U.S. Public Health Service assembled a compilation of available literature on the physiologic effects of fluoride in drinking water, including mottling and cariostasis.[6] Since then, toxicity and adverse health impacts have tested fluoride rather than fluorosilicates. As a recent example, in 2001, the FDA reported that Americans' exposure to fluoride had increased from dentifrices, and it demonstrated that any increases did not produce observable health effects in rats.[7] Fluoride salts were continually tested instead of fluorosilicates because the *complete* and *fast* dissociation−hydrolysis (eq 1) of fluorosilicates to fluoride and (hydr)oxosilicates was generally accepted as a chemical fact. Accordingly, no reason was apparent to test fluorosilicates separately. The completeness and speed of the dissociation−hydrolysis are at the heart of the issue and shall shortly be used to define the scope of this review.

$$H_2SiF_6(aq) + 4H_2O(l) \rightleftharpoons 6HF(aq) + Si(OH)_4(aq) \quad (1)$$

2. Standards for Drinking Water Additives

No federal agency regulates drinking water additives as such. However, the National Sanitation Foundation administers a certification process.[8,9] To be certified, a drinking water additive must contribute less than 10% of the MCL to the finished water supply for any drinking water contaminant regulated by the EPA. The NSF standard always sets this maximum allowable level (MAL) for all additives at 10% of the MCL (post-dilution).[10] The use of NSF-certified or state-certified drinking water additives is mandated by state and/or local authorities in nearly all U.S. states or jurisdictions. Thus, these chemicals are subjected to rigorous standards. Nevertheless, even if drinking water additives were entirely unmonitored, utilities would still be required to meet the NPDWRs as described above for their finished drinking water supplies.

3. Fluoridation Advocacy or Requirement

By law, the EPA is prohibited from recommending fluoride or similar additives for use in PWSs. The EPA may require the addition of a substance to a water supply only to address a deleterious contaminant in the water supply. Further discussion of health, policy, and practical concerns are beyond the scope of this work, but some general comments are instructive. Readers interested in the health and policy aspects are directed elsewhere.[5,6,11,12] Various documents produced by the Centers for Disease Control and Prevention advocate the fluoridation of public water supplies as a public health measure against tooth decay.[13] Some states or lesser governmental authorities require fluoridation within their respective jurisdictions by legislation or administrative action.

4. Available Fluoridation Additives

The most common fluoridating agents used by American waterworks are sodium fluoride (NaF), hexafluorosilicic acid (H_2SiF_6), and sodium hexafluorosilicate (Na_2SiF_6) as shown in Figure 1.[14] Although 25% of the utilities reported using NaF, this corresponds to only 9.2% of the U.S. population drinking

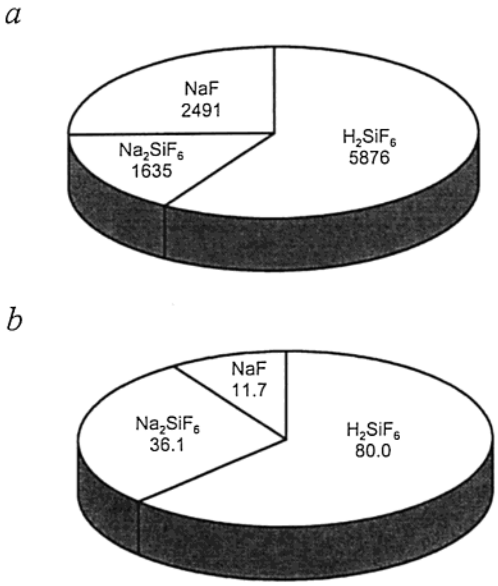


Figure 1. Data for the United States from the CDC's 1992 *Fluoridation Census*: (a) Number of utilities using specific additives as reported by those that fluoridate their water; (b) Populations served by specific additives (millions of people) of those drinking supplementally fluoridated water (does not include waters with naturally occurring fluoride).

fluoride-supplemented tap water. The ease in handling NaF rather than fluorosilicates accounts for the disproportionate use of NaF by utilities serving smaller populations. On the other hand, the cost savings in using fluorosilicates result in large systems using those additives instead. The reduced cost of large volume offsets the costs associated with handling concentrated stocks of the fluorosilicates, which require accommodations similar to hydrochloric acid, which is sometimes used to adjust pH. In acidic solution, the dissociation and hydrolysis of hexafluorosilicic acid, which occurs upon dilution, is given by eq 1. In drinking water, pH is adjusted with the addition of base (e.g., NaOH, $NaHCO_3$); several deprotonations result in the formation of fluoride anion and a mixture of aqueous silicate anions. This also drives the reaction forward.

In the United States, the primary sources of fluoridating agents are rocky mineral deposits containing mixtures of fluorite and apatite; the fluoridating agent itself is produced as a byproduct of phosphate fertilizer manufacture.[15] Both Na_2SiF_6 and K_2SiF_6 occur naturally in volcanic ash as the minerals malladrite and hieratite, respectively.[16−25] Readers interested in the engineering and logistical aspects of fluoridation are referred to manuals by the CDC[26,27] and the American Water Works Association.[28]

5. Definition of Complete and Fast Reaction

This brings us to the next critical issue. For chemists, there are few reactions that are routinely described as complete, e.g., $HCl + NaOH \rightarrow NaCl + H_2O$. Instead, chemists use equilibrium constants to provide a quantitative measure of completeness. Unfortunately, this distinction is lost on the lay public. How far must a reaction go to be described as *complete*? Should it be >99.999%? Should it have an equilibrium constant larger than 10^{20}? Such arguments are not academic if a residual reactant or reaction byproduct is claimed to exert a toxic effect at concentrations in the parts per trillion or lower. Should the *completeness* of reaction then be defined by a sliding scale based on the toxicology of trace residua since health is involved? To bridge the gap between the quantitative language of chemical equilibria and the qualitative language used to address the public, the chemist uses qualifiers, describing the reaction as “virtually complete” or “essentially complete”. Alas, this inexactness leaves uncertainty which, in turn, may allow a potential problem to be overlooked or may be viewed as a weakness in the science by the outsider.

Not only is the equilibrium position of eq 1 important, but the speed with which that equilibrium is achieved is also important. What does *rapid* mean? Over in seconds? Minutes? Does it mean the reaction rate exceeds some set value? Does it mean that the rate constant exceeds some set value? Again, this is not a purely academic argument. What if it takes a certain time for a reactant that is claimed to exert a health effect to be “completely” destroyed? Should a sliding scale be used here? What should it be based on? Perhaps the rate of a reaction should be relative to the time water resides in the treatment plant or based on the time in the distribution system. Maybe the relative magnitude of the reaction rate should be gauged on how long it takes for a particular reactant to fall below a maximum concentration.

C. Scope

There are three sets of interrelated questions that suggest themselves based on the previous discussion, and the majority of this article will be geared toward answering them in alignment with the objectives set above. (1) What residual fluorosilicate species are present at equilibrium? What are the equilibrium constants and the species concentrations? How are the equilibria influenced by the physical and chemical conditions of the system? (2) What new species form during the dissociation and hydrolysis of hexafluorosilicate? What steps are involved in the process? What new species form owing to association/complexation of fluoride or residual fluorosilicates with other species in the water. What are their concentrations? What competition occurs between native and added constituents in a finished water supply? (3) What is the rate at which reaction 1 occurs? Are there quasi-stable intermediates of appreciable concentration? What are the mechanisms and rate laws associated with the processes that take place? What chemical and physical factors affect the rate of the reactions, and what are the magnitudes of such effects?

II. Studies of the Dissociation and Hydrolysis Equilibria

Hexafluorosilicic acid is a strong acid, similar to sulfuric acid (eq 2). However, the second deprotonation, shown in eq 3, is weak with an estimable acid dissociation constant. $K_{a2} = 10^{-0.65}$ using data from Ciavatta,[29] but Sudakova et al.[30] report $K_{a2} = 10^{-1.83}$.

$$H_2SiF_6(aq) \xrightleftharpoons{\text{strong}} HSiF_6^-(aq) + H^+(aq) \qquad (2)$$

$$HSiF_6^-(aq) \xrightleftharpoons{K_{a2} = 10^{-0.65}} SiF_6^{2-}(aq) + H^+(aq) \qquad (3)$$

The hexafluorosilicate anion originates from either hexafluorosilicic acid or its sodium salt in potable water supplies. Upon dilution, the hexafluorosilicate anion dissociates, thereby releasing fluoride ion and producing soluble aquo-, hydroxo-, and oxosilicates. The speciation of aquo-, hydroxo-, and oxosilicates is quite complicated with a number of polymeric species being observed;[31−34] further discussion of those equilibria is beyond the scope of this review. The overall dissociation−hydrolysis process for hexafluorosilicate is shown in eq 4. At the near-to-neutral pHs characteristic of finished drinking water supplies, additional deprotonations can occur, and the net process is best represented by the consumption of base as in eq 5. The pH of a water supply may be adjusted by various means, such as the addition of sodium hydroxide to neutralize acid formed during chlorination, fluoridation, or other treatment steps.

$$SiF_6^{2-}(aq) + 4H_2O(l) \rightleftharpoons 4HF(aq) + 2F^-(aq) + Si(OH)_4(aq) \quad (4)$$

$$H_2SiF_6(aq) + 8OH^-(aq) \rightleftharpoons 6F^-(aq) + SiO_2(OH)_2^{2-}(aq) + 4H_2O(l) \quad (5)$$

The processes represented by eqs 4 and 5 have been studied repeatedly using wet chemical, potentiometric, and spectroscopic methods over a period extending from 1921 to 1988.[29,35−40] However, only the hydrogen fluoride or silicon tetrafluoride molecules and the hexafluorosilicate, bifluoride, and fluoride anions have been definitively observed by ^{19}F NMR or Raman spectroscopy.[41−48] Accordingly, all systems of multiple simultaneous equilibria reported in the literature are based on minimizing the error in fits of experimental (mainly potentiometric) data using practices well-established for the resolution of equilibrium constants. There is considerable debate over the presence of water molecules ligated to silicon(IV) centers. For this reason, the (aq) notation is deliberately retained in the chemical equations to remind the reader that there may be unidentified aquation taking place in intermediates or activated complexes. Virtually all of the research elucidating the partial dissociation and hydrolysis products can be placed into one of three equilibrium system categories. For convenience, these models shall be identified and the number of fluorine atoms present in the fluorosilicate species, so that 4,5,6 means one tetrafluoro-, one pentafluoro-, and one hexafluorosilicate species; 2,6 means one difluoro- and one hexafluorosilicate species; and 1,1,4,6 means two monofluoro-, one tetrafluoro-, and one hexafluorosilicate species.

A. Kleboth's 4,5,6 Model

In 1969, Kleboth studied the fluorosilicate system in 4 M perchloric acid at 25 °C and concluded that the principal species were SiF_6^{2-}(aq), SiF_5^-(aq), and SiF_4(aq), even providing fractional distribution plots of the speciation.[40,49] Beginning in the 1970s, there was considerable interest in hexafluorosilicate dissociation and hydrolysis among Russian investigators. Among them, there appears to have been a general consensus[50−52] of the individual equilibria that occur (eqs 6a−d) but disagreement on the values for the equilibrium constants:

$$HSiF_6^- \rightleftharpoons SiF_6^{2-} + H^+ \quad (6a)$$

$$SiF_6^{2-} + H^+ + H_2O \rightleftharpoons SiF_5(H_2O)^- + HF \quad (6b)$$

$$SiF_5(H_2O)^- + H^+ + H_2O \rightleftharpoons SiF_4(H_2O)_2 + HF \quad (6c)$$

$$SiF_4(H_2O)_2 + 2H_2O \rightleftharpoons Si(OH)_4 + 4HF \quad (6d)$$

Borodin and Zao reported equilibrium constants of 0.025 for eq 6b, 0.004 for eq 6c, and 6.8×10^{-8} for eq 6d.[51] Plakhotnik and Kotlyar[53] reported values of 0.006 (0 °C) and 0.019 (25 °C) for the equilibrium constant of eq 6b; the value at 25 °C compares favorably with that of Borodin and Zao. Plakhotnik[54] reported a value of 0.008 for eq 6d. Plakhotnik drew analogies between the Si^{IV} and the Ge^{IV} fluoride complexes, especially in postulating $SiF_5(H_2O)^-$.[54] It was also speculated that the formation of $HSiF_5$ might account for the solubility of SiO_2 in solutions of H_2SiF_6.[55] Hayek and Kleboth believed that the species $SiF_5(H_2O)^-$ could be deprotonated to give $SiF_5(OH)^{2-}$.[56]

There is some spectroscopic and synthetic evidence to support this system of equations. The system has been studied by ^{19}F NMR spectroscopy;[50,57−59] conditions were quite forcing, with perchloric acid concentrations up to 12 *m* used on some occasions. Buslaev[57] assigned peaks to $SiF_5(H_2O)^-$, $SiF_4(H_2O)_2$, and a new species $SiF_3(OH)(H_2O)_2$. The reaction was expressed in the rather unusual form of eq 7 when $[Si^{IV}]/[F^-] \approx 5$:

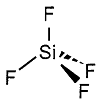
$$20SiO_2(aq) + 102HF \rightleftharpoons 5.5SiF_6^{2-} + 12SiF_5(H_2O)^- + 1.3SiF_4(H_2O)_2 + 1.2SiF_3(OH)(H_2O)_2 \quad (7)$$

Equation 7 is not balanced, except with respect to silicon(IV). The fluoride may be balanced by changing the HF coefficient on the left-hand side to 101.8, which suggests a simple rounding error or their desire not to use 4 significant digits, since the speciation is based on spectral data. It appears that the authors' intention was to exclude water and hydrogen ions. The addition of 21.8 water molecules to the right-hand side to balance the oxygen (oxide) counts still leaves a discrepancy in the hydrogen ion counts, with 23.2 additional hydrogen ions needed on the right-hand side. Since the authors did not measure acidity and water was the solvent, it is reasonable to assume that they intended to convey information only about the fluorosilicate speciation and purposely left the equation unbalanced.

Kleboth and Rode concluded that all the postulated species were stable by using ab initio calculations.[60] In the gas phase, the fluoride affinity of SiF_4 has been determined as a measure of its Lewis acidity, which falls between BrF_3 and SeF_4;[61] it does not appear that the fluoride affinity of SiF_5^- has been determined even though SiF_6^{2-} is stable. In addition, several pentafluorosilicate species have been synthesized, isolated, and/or characterized in the solid state.[62−66] A significant number of stable pentacoordinate heteroleptic fluorosilicates exist;[67−71] therefore, it is not possible to summarily dismiss the reasonableness of silicon(IV) species with five (mixed) ligands. Some, such as $[S(N(CH_3)_2)_3^+][Si(CH_3)_3F_2^-]$, find use as polymerization catalysts,[72] while others, such as $[HSi(OCH_2CH_3)_4^-]$, are excellent one-electron reductants.[73] In $[As(C_6H_5)_4][SiF_5]$ and [*trans*-$PtCl(CO)(P(C_2H_5)_3)_2$][SiF_5], the pentafluorosilicate ion is pentacoordinate without an aquo ligand.[62,63] However, a bridging oxo ligand completes the hexacoordinate geometry in $[As(C_6H_5)_4^+]_2$ $[F_5SiOSiF_5^{2-}]$;[62] consequently, it is unclear whether the presence of aquo ligands should be assumed to fix the coordination number at six in the aqueous phase. In the case of hydroxosilicates (silicic acids), the pentacoordinate species, $Si(OH)_5^-$, is predicted to be the most stable in the gas phase, with $Si(OH)_4$ acting as a Lewis acid; this contrasts with aqueous-phase NMR studies that show $Si(OH)_4$ acts as a Brønsted–Lowry acid and is deprotonated to form $SiO(OH)_3^-$ because this species is stabilized by hydration.[33] (Gas-phase studies of many organosilanes have been reviewed elsewhere.[74]) Such a result may suggest that SiF_5^- is substantially aquated and may not exist except as the hexacoordinate species, $SiF_5(H_2O)^-$, or may be destabilized so that loss of a fluoride is promoted, yielding an aquated SiF_4 species. The existence of SiF_5^- has been verified by both NMR spectroscopic[66] and X-ray crystallographic studies.[63,65] There are also ^{19}F NMR and IR spectroscopic data to show that tertiary organic ammonium salts of SiF_5^- exist.[75–78] Accordingly, despite theoretical objections,[79,80] there would appear to be little doubt that the pentafluorosilicate anion exists. To what extent it occurs in aqueous solution—where the addition of an aquo ligand is possible—is another matter entirely, of course. The chemistry of fluorides of penta- and hexacoordinate silicon(IV) has been reviewed previously.[81–83]

The tetrafluoro species represented simply as SiF_4(aq) is not merely dissolved silicon tetrafluoride (tetrafluorosilane) gas but an aquated species—or possibly multiple aquated species with four fluoride ligands each.[49,84] Kleboth called it both *tetrafluorosilicic acid* and *silicon tetrafluoride dihydrate*, referring to it as an adduct, $SiF_4{\cdot}2H_2O$.[49] Such a species is probably best named as diaquotetrafluorosilicon(IV) more akin to a hydrated metal complex, and it has been observed by infrared spectroscopy in the solid phase.[85] Hayek and Kleboth also believed that $SiF_4{\cdot}2H_2O$ could be doubly deprotonated to give what is essentially an adduct composed of one silicon tetrafluoride molecule and two hydroxide anions.[56] A number of oxygen or nitrogen Lewis bases form 1:1 and/or 2:1 complexes with SiF_4, including ammonia ($SiF_4{\cdot}NH_3$; $SiF_4{\cdot}2NH_3$), benzimidazoles ($SiF_4{\cdot}2N{-}Bz$), water ($SiF_4{\cdot}H_2O$), methanol [$SiF_4{\cdot}CH_3OH$], and methyl ether [$SiF_4{\cdot}(CH_3)_2O$] as well as [$SiF_3(OCH_3)$], which forms upon reaction with methanol and loss of HF.[85–90] Just how stable $SiF_4(H_2O)_2$ should be is debatable, and assertions of its omnipresence in aqueous solutions of hexafluorosilicate salts has been challenged using cryoscopy (molal freezing point depression).[91] The infrared spectrum of SiF_4 gas is reported in the literature;[48] therefore, comparison of gas- and aqueous-phase spectra may provide some information about the nature of aquation.

While the presence of the two water molecules may have little significance from the standpoint of an equilibrium expression, aquation in the ligand sphere may influence the rate of the subsequent steps of the substitution/hydrolysis for several reasons. (1) The symmetry is markedly different. Tetrafluorosilane **1** is T_d. Presumably, $SiF_4(H_2O)_2$ is D_{4h} with the water molecules in a trans orientation **2**, but C_{2v} with a cis orientation is also possible **3**. (2) The Si–F bond lengths are probably different (longer). (3) The sterics suggest (probably require) that hexafluorosilicate decomposition begin with a dissociative rather than associative step because the coordination number of the silicon center is at its maximum. Concerted or consecutive loss of H^+ and F^- (or vice versa) from 2 or 3 begins to form the Si–OH moieties of the silicic acid product. (4) The water molecules can undergo facile H^+ loss or gain, thus affording a mode for rapid changes in net charge as well as ligand composition, which in turn affects the ability to serve as leaving groups.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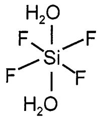
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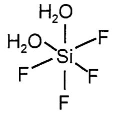
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B. Busey's 2,6 and 2,4 Models

In 1980, the hexafluorosilicate system was studied potentiometrically by Busey et al. in NaCl solution.[36] They concluded that the process was represented by the following equilibria in aqueous solution (eqs 8a–c). Note that eqs 8b-1 and 8b-2 are intended to represent speciation fits of temperature-dependent experimental data and are not suggested to occur simultaneously.

$$SiF_6^{\,2-} + 4H_2O \xrightleftharpoons{K = 10^{-29.98}} Si(OH)_4 + 6F^- + 4H^+ \text{ at } 25\ {}^\circ C \quad (8a)$$

$$SiF_6^{\,2-} + 2H_2O \xrightleftharpoons{K = 10^{-18.89}} Si(OH)_2F_2 + 4F^- + 2H^+ \text{ at } 25\ {}^\circ C \quad (8b\text{-}1)$$

$$SiF_6^{\,2-} + H_2O \xrightleftharpoons{K = 10^{-10.20}} Si(OH)F_4^- + 2F^- + H^+ \text{ at } 0\ {}^\circ C \quad (8b\text{-}2)$$

A different model was employed at 0 °C than at 25 °C because the data fit the alternative model better. In the low-temperature model, they replaced eq 8b-1 with eq 8b-2; the value of the equilibrium constant for eq 8a then became $10^{-31.61}$. While statistically valid, this is rather unsatisfying from a physical inorganic chemistry standpoint as no chemical rationale was offered other than goodness of fit. It also offers no information about intermediate temperatures that are relevant to potable water systems because their piping is exposed to seasonal and meteorological temperature influences. Golovnev studied the effect of ionic strength on the HF acid dissociation constant and the equilibrium constant for eq 8a (Table 1) and confirmed the values found by Busey et al.[92] That a pentafluorosilicate species was not included is somewhat

Table 1. Effect of Ionic Strength on the Equilibrium Constants for HF Dissociation and SiF_6^{2-} Dissociation–Hydrolysis (from Golovnev[92])

μ, M (as NaCl)	HF pK_a	pK for eq 7a
0	3.16	30.02
0.1	2.97	29.48
0.2	2.93	29.43
0.4	2.92	29.50
0.6	2.91	
0.8	2.92	29.70
1.0	2.94	29.94
2.0	3.02	30.88
3.0	3.28	32.33

surprising given the spectroscopic and solid structure (of synthesized compounds) evidence for both the solvated and the unsolvated SiF_5^- ion. In addition, the absence of a tetrafluorosilicon(IV) species appears to be inconsistent with the fact that tetrafluorosilane gas exists and would presumably be hydrated if dissolved into an aqueous solution. While a number of nitrogen or oxygen Lewis base adducts of SiF_4 are known (vide supra), it is still unknown whether SiF_4 (or some adduct) would be stable in excess water.

C. Ciavatta's 1,1,4,6 Model

In 1988, Ciavatta et al. studied the reaction potentiometrically.[29] They fitted their data to the following set of reactions, all aqueous species:

$$HSiF_6^- \xrightleftharpoons{K_{a2} = 10^{-0.65}} SiF_6^{2-} + H^+ \quad (9a)$$

$$SiF_6^{2-} + 2H^+ \xrightleftharpoons{K = 10^{-3.88}} SiF_4 + 2HF \quad (9b)$$

$$SiF_6^{2-} + 3H^+ + 2H_2O \xrightleftharpoons{K = 10^{-11.57}} Si(OH)_2F^+ + 5HF \quad (9c)$$

$$SiF_6^{2-} + 2H^+ + 3H_2O \xrightleftharpoons{K = 10^{-10.83}} Si(OH)_3F + 5HF \quad (9d)$$

$$SiF_6^{2-} + 2H^+ + 4H_2O \xrightleftharpoons{K = 10^{-13.23}} Si(OH)_4 + 6HF \quad (9e)$$

Although they mentioned previous work that was not in agreement, they did not try to rationalize their choices for species except on the basis of the fit to the potentiometric data. This particular system of simultaneous equilibria is the only one that includes a cationic silicon(IV) species, $Si(OH)_2F^+$. Presumably, the species is hydrated with three aquo ligands, but the authors did not address that matter. Like Kleboth's system, this one includes a tetrafluorosilicon(IV) species. The solvation sphere is unspecified but probably should include two aquo ligands. Like Busey's system, this one excludes a pentafluorosilicate species, which again seems to be inconsistent with the several reports documenting the existence of this anion.

D. Other Equilibrium Studies

Roberson and Barnes suggested that an additional weak fluorosilicon(IV) complex besides SiF_6^{2-} was present.[80] They speculated it might be $Si(OH)_3F$ or $Si(OH)_4F^-$ but felt that the data could not be used to unequivocally establish its presence. Initially, they assumed that a consecutive, cumulative series of fluoro complexes existed, but eventually were forced to reject that hypothesis based on the data they obtained. When the average ligand number $\bar{n}$ (molar ratio of silicon-bound fluoride to total silicon) ranged from 0.2 to 6, it was concluded that SiF_6^{2-} was the major species. However, they studied the reaction only near pH 4. They did fix the ionic strength to 0.1 M with $NaNO_3$, NaCl, or $NaClO_4$, unlike many other works where ionic strength was permitted to fluctuate under the influence of the reactants and products. Their total silicon(IV) concentrations ranged from 2.5 to 5.0 mM (10–20× a reasonable drinking water concentration of 0.3 mM). Their concentrations of total fluoride (0.10–40 mM) were some 2–800× drinking water concentrations (53 μM for 1 ppm); consequently, the statement regarding speciation as a function of $\bar{n}$ is not necessarily valid because the higher concentrations of both fluoride and silicon(IV) would force the product distribution away from hydroxo complexes in favor of fluoro complexes.

The reaction was also studied by Crosby.[37] Crosby's principal concern was whether a sufficient level of fluoride was maintained. Once he was convinced that more than 95% of the hexafluorosilicate had been converted to fluoride, he did not pursue refinements to determine the residual hexafluorosilicate because 0.95 ppm of fluoride is close enough to 1 ppm of fluoride in terms of ensuring the presence of free fluoride. In fact, Crosby begins his paper by discussing several fluoridated compounds and whether they will release fluoride in the mouth. The equilibrium was similarly studied by Cooke and Minski, who also geared their experiments toward showing that a sufficient quantity of fluoride was released into the solution.[93] They calculated an equilibrium constant for the formation of aqueous silicon tetrafluoride (eq 9b) and found that it varied as a function of the initial concentration of Na_2SiF_6. This result was inconsistent with previous studies, which showed only scatter (as they pointed out). Such variation—if in fact correct—is probably due to unaccounted for subsequent or simultaneous equilibria.

The dissociation and hydrolysis of magnesium hexafluorosilicate was also studied.[94] The investigation used a buffer based on 5 mM sodium 5,5-diethylbarbiturate and followed the fluoride generation with an ion-specific electrode upon the addition of 0.50 or 0.10 mM $MgSiF_6$. The initial pH (before addition of the $MgSiF_6$ solid) was adjusted to 7.4, the buffer's pK_a. The authors reported only 60% release of the fluoride. The validity of this result may be challenged for two reasons. First, it is not clear if the buffer capacity is sufficient for this amount of acid. Each hexafluorosilicate ion generates four hydrofluoric acid molecules. For the hydrolysis of the lower concentration of SiF_6^{2-} (0.10 mM), the resulting concentration of HF was 8.0% of the total buffer concentration (and 16% of the basic form, which was immediately protonated); therefore, the hydrolysis reaction shifted the pH (the authors did not monitor the pH). Second, in addition to the Mg^{2+} in the salt, the buffer also contained 0.5 mM Mg^{2+} and 0.15 mM Ca^{2+}. Both of these metal cations form fluoride complexes, thus reducing the free fluoride concentration. It is not clear if they would also have interfered with the chemosensor (i.e., electrode surface). Third, a small portion of the silicic acid formed by the reaction would also contribute acidity, further lowering the pH. This explanation (especially the increase in acidity) appears to be supported by the experimental data, which showed reduced relative fluoride production (i.e., lower fractional dissociation) at the higher initial concentration of $MgSiF_6$.

III. Fractional Speciation

A. Fractional Distributions under Drinking Water Conditions

The only matter generally agreed upon among those who have studied fluorosilicate formation or dissociation is that there is no series of species resulting from consecutive, cumulative substitutions of hydroxide for fluoride.[29,36,80,95] In other words, there is no consecutive series of complexes of the form $[SiF_m(OH)_n]^{4-m-n}$ with $m + n \leq 6$ and their associated protonations and deprotonations. As noted above, only the hexafluorosilicate anion itself has been indisputably identified in aqueous solution. As a consequence, the equilibrium is generally represented in terms of a net process where the hexafluorosilicate molecule is totally decomposed to a silicic acid molecule, four hydrogen cations, and six fluoride anions. For example, Gmelin[95] tabulates values for the constant represented by eq 10. The values range from a minimum of $10^{28.23}$ to a maximum of $10^{31.61}$; some of these values have been summarized in Table 2. However, relying on equilibrium constants for eqs 6b–d from Borodin and Zao[51,58] and pK_a from Mesmer and Baes,[96] we arrive at a value of 9.1×10^{16}, which is still large but substantially different from the other values reported in the literature.

Table 2. Values of the Equilibrium Constant for eq 10 at 25 °C as Tabulated by Gmelin[95]

log *K*	μ^a	ref	log *K*	μ^a	ref
30.02	0	38,92	29.94	1.0	38,92
30.35	0	137	30.88	2.0	38,92
30.18	0.10	80	32.33	3.0	38,92
31.08	0.20	138	30.8	unspec	36[b]
29.50	0.40	38,92	29	unspec	36[c]
29.98	1.0	36			

[a] The symbol μ represents ionic strength; unspec = unspecified. [b] Busey et al.[36] calculated this value from data given by Crosby.[37] [c] Busey et al.[36] calculated this value from data given by Kubelka and Přistoupil.[35]

$$K = \frac{[SiF_6{}^{2-}]}{[Si(OH)_4][H^+]^4[F^-]^6} \qquad (10)$$

When hexafluorosilicate anion dissociates, releasing fluoride ion, there is insufficient evidence to demonstrate that the silicon(IV) center maintains a coordination number of six, but it has generally been presumed to do so, with water molecules displacing the fluoride. Regardless of model, the equilibrium constants resolved for this system are all macroscopic in nature. In other words, they are based on species with the general compositions given in the individual reactions, but without regard to structure and bonding. Because fluoride forms strong hydrogen bonds, some researchers have postulated that hydrogen-bonded species such as $F\cdots H-F-SiF_4(H_2O)^-$ may exist in addition to or instead of $H-F-SiF_5{}^-$. Therefore, the elucidation of residual species is further complicated from an isomeric standpoint. Such concerns may seem rather academic, but toxicological and pharmacological properties are normally influenced by structure in addition to composition. Accordingly, it is possible for structural isomers to vary in physiologic activity so that the species which dominates the biology is not the one whose concentrations dominates in solution. Despite these general truths, it is not clear whether the toxicological and pharmacological properties of these specific species are affected by isomerism.

In addition to the fluorosilicate equilibria, there are a number of equilibria involving fluoride with other species. Two equilibria that can be found in any aqueous system containing fluoride are the formation of hydrofluoric acid and bifluoride anion, shown in eqs 11a,b.[96] Slightly different values for these constants may be found elsewhere.[97] (Gas-phase data also exist on the stability of hydrogen bonded fluorospecies.[98]) In addition, silicic acid has two dissociations, given in eqs 12a,b, which must be included.[99]

$$F^- + H^+ \xrightleftharpoons{K = 10^{2.887}} HF \qquad (11a)$$

$$2F^- + H^+ \xrightleftharpoons{K = 10^{3.87}} HF_2{}^- \qquad (11b)$$

$$Si(OH)_4 \xrightleftharpoons{K = 10^{-9.83}} SiO(OH)_3{}^- + H^+ \qquad (12a)$$

$$Si(OH)_4 \xrightleftharpoons{K = 10^{-23.0}} SiO_2(OH)_2{}^{2-} + 2H^+ \qquad (12b)$$

The hexafluorosilicate anion is stable only in a narrow pH range. As Katorina et al. reported, "In strongly acidic solutions, the stability of the [hexa]-fluorosilicate ion is lowered, and it is completely decomposed in 0.025 M or 0.050 M H_2SO_4 at concentrations of 0.15 mM or 0.2 mM Na_2SiF_6".[100] In an interesting twist, hexafluorosilicate is destroyed in concentrated, strong acid due to the formation of the weak acid HF and in base due to the formation of silicic acid and eventually oxosilicates. This point was observed by Golovnev, who noted the apparent discrepancies in the literature and calculated that the hexafluorosilicate anion is most stable around pH 2.6.[38] In concentrated solutions (e.g., stock commercial solutions may contain 20% w/w), dimerization occurs. The dimer can then lose two HF molecules.[101]

$$2H_2SiF_6 \rightleftharpoons (H_2SiF_6)_2 \rightleftharpoons H_2Si_2F_{10} + 2HF \qquad (13)$$

It is sometimes suggested that the dimer $(H_2SiF_6)_2$ actually exists as a hydrogen-bonded form with at least one but possibly two bridging fluoride ligands, perhaps something like $(FHF)(HF)F_2Si(\mu\text{-}F)_2SiF_2(FH)(FHF)$. There are also so-called "high silica fluosilicic acids" that are believed to contain a species called fluodisilicic acid, often represented as $[SiF_6 \cdot SiF_4]^{2-}$,[56,102,103] but that is probably better represented as $[SiF_4(\mu\text{-}F)_2SiF_4]^{2-}$. It should be noted that the empirical formula of the parent acid is $HSiF_5$, which was previously proposed upon the dissolution of SiO_2 in hexafluorosilicic acid[55] and whose deprotonated anion was proposed as an intermediate in the dissociation–hydrolysis of hexafluorosilicic acid (vide supra). Harris and Rudner disputed that polymerization occurs, as opposed to formation of $HSiF_5$;[77] however, they also felt that $Si_2F_{11}^{3-}$ and $Si_3F_{16}^{3-}$ could form in the presence of tertiary ammonium cations.[78] The existence of bridging fluoride ligands has been strongly debated, and different interpretations of the spectroscopic evidence have been put forth.[78,104] Ennan et al. felt that the infrared and ^{19}F NMR spectra supported the existence of only SiF_6^{2-} and SiF_5^- in solution.[104]

There is some speculation offered by Roberson and Barnes,[80] but the reference to varying bond strengths of Si–F and Si–O bonds in minerals is unsatisfying. Regardless of the reasons for the instability of step-by-step replacement of fluoro ligands for hydroxo ligands, it is a stark contrast to metal–ligand complexes where consecutive additions or substitutions of a ligand are commonplace. Unfortunately, there is not agreement on what species actually exist, especially the heteroleptic species. Therefore, the only option is to compare and contrast the speciation predicted for an individual model, given the current state of the science. The more recent studies by Busey et al.[36] and Ciavatta et al.[29] were used for this purpose. The total fluoride concentration was set at $[F^-]_T = 19\ \mu M$ (1 mg L^{-1}), which represents a typical level as the EPA's secondary MCL is twice that. Soluble silicates are present in natural waters and are dissolved from the surrounding minerals as the water passes over them. In fact, some of these very same waters naturally contain fluoride.[80] Regardless of the source of silicon(IV), i.e., anthropogenic or native, the addition of any fluoridating agent results in similar speciation because the dissolved silica concentration is essentially unchanged by the addition of the agent (but usually all the fluoride comes from the agent). In other words, the dissolved silica contribution of the fluoridating agent is trivial compared to the native silica. Silicate concentrations can vary widely as they are strongly influenced by the minerals to which the water is exposed as well as temperature. However, a typical total silicate concentration was selected for these calculations: $[Si^{IV}]_T = 300\ \mu M$ (18 mg L^{-1} as SiO_2); this is about 95× the $[Si^{IV}]$ present from the hexafluorosilicate additive itself, so that the hexafluorosilicate contribution to $[Si^{IV}]_T$ is negligible.

Fractional distribution plots were constructed for both Busey's 2,6 and Ciavatta's 1,1,4,6 fluorosilicate speciation models using a specialty software package, MINEQL+ version 4.0 (Environmental Research Software, Hallowell, ME). These plots illustrate the speciation of the silicon(IV) as a function of pH. No corrections or adjustments for ionic strength or temperature were made, and so these figures are approximations. Dimeric or other polymeric species were likewise excluded, given the dilute nature of the drinking water system, but the equilibria shown in eqs 11 and 12 were included. As is readily apparent from examination of Figures 2 and 3, which are based on the Busey[36] and Ciavatta[29] models, respectively, the concentrations of any fluorosilicate species are extremely small at drinking water pH. This reaffirms the statement made by Feldman et al. in 1955 (when they presented the work):[3] The equilibria needed for the calculation of fractional speciation are summarized in Tables 3–5.

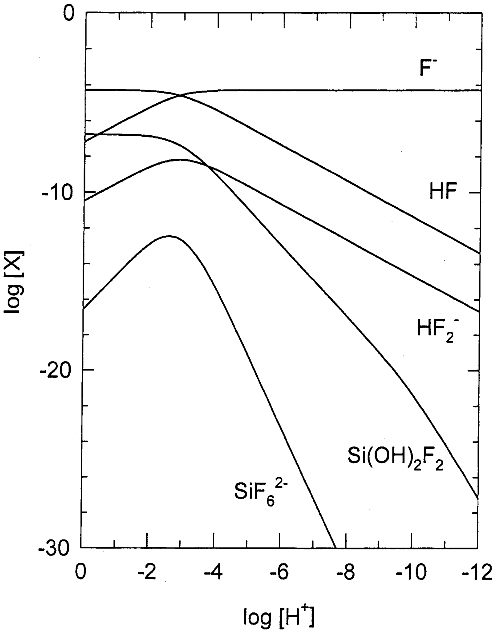

Figure 2. Fractional distribution plot is shown for fluoride species as a function of pH based on Busey's 2,6 model at 25 °C; $[Si^{IV}]_T = 300\ \mu M$ (18 mg L^{-1} as SiO_2) and $[F^-]_T = 19\ \mu M$ (1 mg L^{-1}).

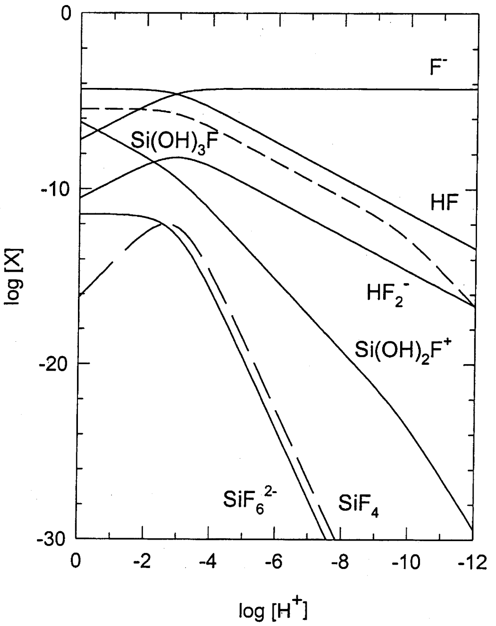

Figure 3. Fractional distribution plot is shown for fluoride species as a function of pH based on Ciavatta's 1,1,4,6 model; $[Si^{IV}]_T = 300\ \mu M$ (18 mg L^{-1} as SiO_2) and $[F^-]_T = 19\ \mu M$ (1 mg L^{-1}).

It is concluded that in any drinking water supply with a pH of 5 or higher, fluoridated with sodium silicofluoride [hexafluorosilicate] to the extent of 16 ppm of F or less, all of the silicofluoride is completely hydrolyzed to silicic acid, fluoride ion, and hydrogen

Table 3. Systems of Simultaneous Equilibria (and their Constants) Proposed for the Hexafluorosilicate Dissociation−Hydrolysis Reaction in Aqueous Solution

reaction	log *K*	ref
Scheme 1 (Kleboth's 4,5,6 Model)		
$HSiF_6^- \rightleftharpoons SiF_6^{2-} + H^+$	unreported	40,49
$SiF_6^{2-} + H^+ + H_2O \rightleftharpoons SiF_5(H_2O)^- + HF$	−1.60	51
	−1.72	53
$SiF_5(H_2O)^- + H^+ + H_2O \rightleftharpoons SiF_4(H_2O)_2 + HF$	−2.4	51
$SiF_4(H_2O)_2 + 2H_2O \rightleftharpoons Si(OH)_4 + 4HF$	−7.17	51
	−2.1	54
Scheme 2a (Busey's 2,6 Model @ 25 °C)		
$SiF_6^{2-} + 4H_2O \rightleftharpoons Si(OH)_4 + 6F^- + 4H^+$	−29.98	36
$SiF_6^{2-} + 2H_2O \rightleftharpoons Si(OH)_2F_2 + 4F^- + 2H^+$	−18.89	
Scheme 2b (Busey's 4,6 Model @ 0 °C)		
$SiF_6^{2-} + 4H_2O \rightleftharpoons Si(OH)_4 + 6F^- + 4H^+$	−31.61	36
$SiF_6^{2-} + H_2O \rightleftharpoons Si(OH)F_4\text{-} + 2F^- + H^+$	−10.20	
Scheme 3 (Ciavatta's 1,1,4,6 Model)		
$HSiF_6^- \rightleftharpoons SiF_6^{2-} + H^+$	−0.65	29
$SiF_6^{2-} + 2H^+ \rightleftharpoons SiF_4 + 2HF$	−3.88	
$SiF_6^{2-} + 3H^+ + 2H_2O \rightleftharpoons Si(OH)_2F^+ + 5HF$	−11.57	
$SiF_6^{2-} + 2H^+ + 3H_2O \rightleftharpoons Si(OH)_3F + 5HF$	−10.83	
$SiF_6^{2-} + 2H^+ + 4H_2O \rightleftharpoons Si(OH)_4 + 6HF$	−13.23	

Table 4. Equilibrium Constants for Formation of Hydrogen Fluoride and Bifluoride in Aqueous Solution

	log *K*	
reaction	value from ref 96	value from ref 97
$F^- + H^+ \rightleftharpoons HF$	2.887	2.94
$2F^- + H^+ \rightleftharpoons HF_2^-$	3.87	3.56

Table 5. Cumulative Dissociation Constants for Silicic Acid from Nordstrom et al.[99]

reaction	log *K*
$Si(OH)_4 \rightleftharpoons SiO(OH)_3^- + H^+$	−9.83
$Si(OH)_4 \rightleftharpoons SiO_2(OH)_2^{2-} + 2H^+$	−23.0

fluoride. There can be no question of toxicity of SiF_4 or SiF_6^{2-} under such conditions.

B. Influences of Metal Cations on Fluoride Speciation

Natural waters contain a number of metallic cations that can be ligated by fluoride. Fluoride binds to trivalent metal cations, such as iron(III) and aluminum, as well as divalent metal cations, such as calcium and magnesium.[105] This point was not lost on Feldman et al. back in 1955.[3] They considered 29 different metal cations that might influence fluoride concentrations, either through complexation or precipitation. In 1985, Pitter expressed concern that the formation of fluoro complexes of Al^{3+} was lowering the free fluoride concentration below the optimal levels for dental health benefits.[106] Much of the fluoride is in fact present as metal complexes, depending on the concentrations of the metal cations, the fluoride anion, and the hydrogen ion. The stability constants for these complexes have been tabulated previously, and the effects of the metal cations fractional distribution plots have been taken into account so they will not be repeated here.[2] The pH determines the degree of hydrolysis (hydroxo-complexation) of the metal cations, thereby indirectly affecting the concentration of free fluoride ion owing to competition between the hydroxide and the fluoride for the metal cations. In general, constants have not been reported for heteroleptic fluorohydroxo metal complexes, and such species are largely unstudied. In a few cases, such as aluminum(III), significant inroads have been made on mixed fluorohydroxo complexes.[107−111]

Formation of complexes also influences the solubilities of fluoride-bearing minerals in hydrogeologic settings.[112,113] The difficulties associated with the synthesis of hexafluorosilicates of Al^{3+}, Fe^{3+}, Zr^{4+}, and UO_2^{2+} led to the conclusion that hexafluorosilicate is decomposed by cations that form strong fluoro complexes.[114] When dissolved in water, $CaSiF_6$ dissociates to Ca^{2+} and SiF_6^{2-} but the hexafluorosilicate is hydrolyzed upon dilution of the solution, giving silicic acid, hydrofluoric acid, and a precipitate of calcium fluoride.[91] Later work contradicted the data on UO_2^{2+} and also showed that NpO_2^{2+} and PuO_2^{2+} complexes with hexafluorosilicate could be formed in aqueous solution; the stability constants range from 25 to 252, depending on the actinide and conditions.[114]

Not only does the formation of fluoro complexes reduce the concentration of free fluoride and fluorosilicates, but it can have practical consequences for other treatment processes. If fluoride is injected before or during alum coagulation, fluoridation can impair the process, which relies on hydroxo complexation and flocculation of insoluble hydroxides.[115,116] This is readily apparent when examining the impact of fluoride on the turbidity of an Ohio River water sample undergoing coagulation.[115] Figure 4 shows how the effectiveness of alum coagulation is reduced by the addition of fluoride. The turbidity of the water rises sharply every time a dose of fluoride is added. In addition, the turbidity never drops to the level of the control stream, to which no fluoride was added. Consequently, the addition of fluoride to the water stream prior to coagulation is contraindicated since it increases the alum dose required to achieve the same level of turbidity reduction as shown by Figure 5. In many treatment plants it is not uncommon for fluoride to be added early on. Such practices result in costlier operation due to increased coagulant consumption and may result in higher concentrations of the metal cation (Fe^{3+} or Al^{3+}) in some finished water supplies than if the fluoride were added post-coagulation. The observations suggest that there is considerable competition between the fluoride and the hydroxide for the aluminum and possibly heteroleptic complexation or fluoride occlusion.

One of the issues sometimes raised with regard to the use of sodium hexafluorosilicate and hexafluorosilicic acid as fluoridating agents—as opposed to sodium fluoride—is whether residual hexafluorosili-

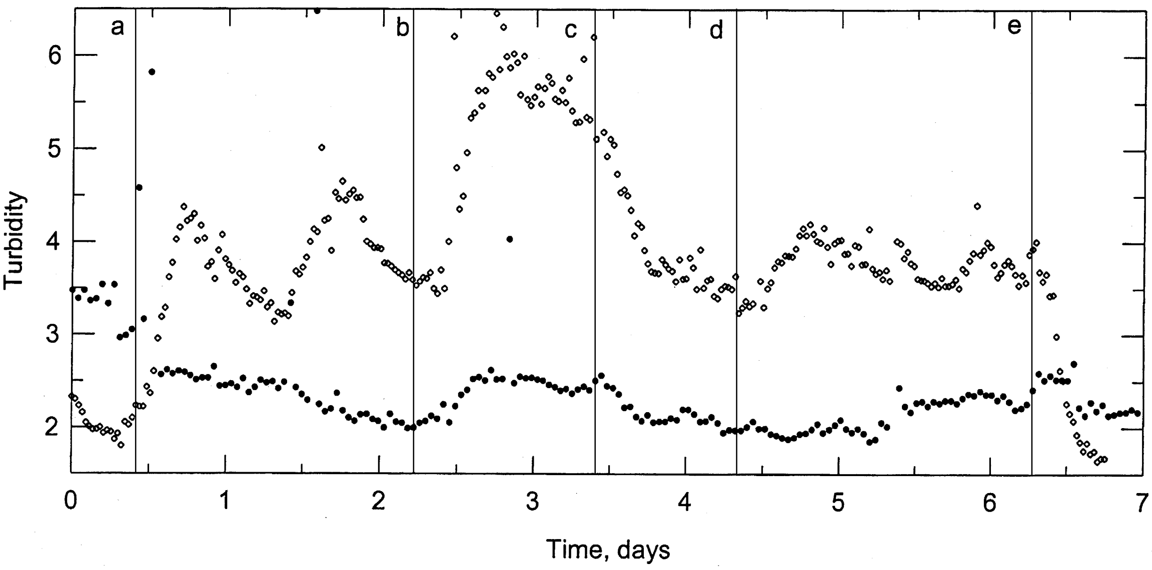

Figure 4. Fluoride addition lowers the effectiveness of coagulation with alum, $KAl(SO_4)_2 \cdot 12H_2O$: (●) Turbidity of the control, operated with 63 μM alum; (○) How the addition of fluoride reduces the effectiveness of alum at lowering turbidity. Time points represent postmixing concentrations after injections of fluoride and/or alum: (a) $[F^-]_T = 38\ \mu M$, $[Al^{III}]_T = 63\ \mu M$; (b) $[F^-]_T = 38\ \mu M$, $[Al^{III}]_T = 46\ \mu M$; (c) $[F^-]_T = 38\ \mu M$, $[Al^{III}]_T = 63\ \mu M$; (d) $[F^-]_T = 76\ \mu M$, $[Al^{III}]_T = 63\ \mu M$; (e) $[F^-]_T = 0\ \mu M$, $[Al^{III}]_T = 63\ \mu M$. Conversions: for fluoride, 19 μM = 1 mg L^{-1}, FW = 19 g mol^{-1}; for alum, 63 μM = 30 mg L^{-1}, FW = 474 g mol^{-1}. Data have been adapted from Feld et al.[115]

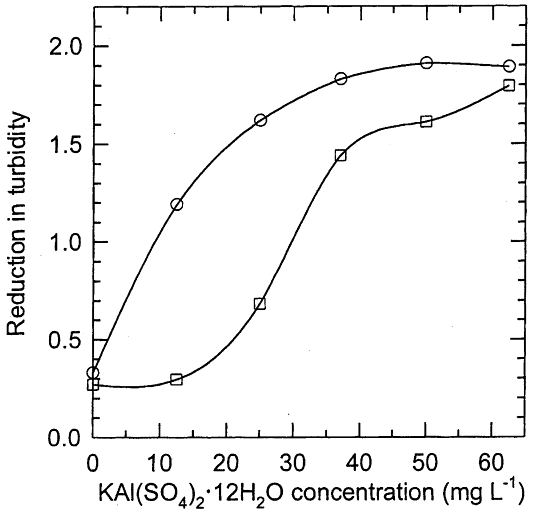

Figure 5. Efficiency of alum coagulation is reduced by fluoride. Almost twice as much alum is required to achieve the same reduction in turbidity in the presence of fluoride ($[F^-]_T = 19\ \mu M = 1$ mg L^{-1}) at alum concentrations up to 30 mg L^{-1} (63 μM). Data have been adapted from Feld et al.[115]

cate anion can form ingestible complexes with metal cations.[117] This matter has previously been considered in some detail,[2] but there are three key points worth noting here. First, the only available data on hexafluorosilicate complexes or ion pairs suggests that they are very weak and can only form in concentrated solution.[118] In fact, the complexes are entirely outer sphere; the evidence suggests there is no linkage at the molecular scale, only an ion pair. Second, hexafluorosilicates of several metals (Na^+, Mg^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}) have been synthesized and purified.[119] Other than Na_2SiF_6, the others all formed with waters of hydration. In the hexafluorosilicate salts, Mg^{2+} and Zn^{2+} precipitated as hexaaquo ions while Pb^{2+} and Cu^{2+} precipitated as tetraaquo ions. The aquo ligands completely fill the coordination spheres of the metal cations, showing that in the solid there is only a simple electrostatic interaction holding the two ions together as a salt and not an inner-sphere link (such as a bridging fluoro ligand). It has also been noted that SiF_6^{2-} forms only outer-sphere complexes, even with polarizable species such as Ag^+.[120] Even in the solid phase, anhydrous K_2SiF_6 shows only an ionic bond (no dative bonds, only electrostatic interactions). In fact, the symmetry about the central silicon is O_h, unlike the GeF_6^{2-} or SnF_6^{2-} compounds where it becomes D_{3d}.[121] Third, the fact that these compounds may be synthesized (especially $[Pb(H_2O)_4][SiF_6]$) means that they could be directly dissolved into water to test for the existence of association complexes. Interestingly, tetraaquolead(II) hexafluorosilicate decomposes in moist air, producing PbF_2 among other things.[119]

IV. Kinetics

A 1958 review says the reaction (eq 4) is slow in cold basic solution.[122] Another reports the reaction "produc[es] fluoride ions very slowly".[123] Nevertheless, most of the equilibrium studies and the modest kinetic studies suggest it is actually rather facile. It largely appears to depend on what rate or rate constant is described as *slow*.

The net dissociation–hydrolysis (eq 4) has been reported to be first order and unaffected by base,[124] with the very first dissociation of a fluoride ion proposed as the rate-limiting step (eq 14), which results in a differential rate expression reminiscent of an S_N1 reaction, which is how this system can be viewed if addition of a hydroxide or water molecule follows the loss of the fluoride (eq 15). It is worth mentioning that the S_N1 reactions encountered in organic chemistry usually are viewed as having a rapid equilibrium that forms the reactive species (e.g., a *tert*-butyl chloride molecule dissociating to form a *tert*-butyl carbocation and a chloride anion).

$$SiF_6^{2-}(aq) \xrightarrow{k_1} SiF_5^{-}(aq) + F^{-}(aq) \quad (14)$$

$$-d[SiF_6^{2-}(aq)]/dt = k_1[SiF_6^{2-}(aq)] \quad (15)$$

It is unclear whether there is a water molecule datively bound to the pentafluorosilicate anion on the right-hand side of eq 14. It is difficult to imagine eq 14 is irreversible as written, as opposed to a rapid equilibrium (eq 16a) or a fast reversible reaction (eq 16b). In either case, the resulting differential rate expressions are potentially consistent with the literature data due to the design of the kinetics experiments conducted. If eq 17 is taken to be the subsequent step in the mechanism, the differential rate expressions that follow from eqs 16a and 16b are eqs 19a and 19b, respectively (a steady state in the concentration of SiF_5^- is assumed for eq 19b, i.e., $d[SiF_5^-]_{ss}/dt \approx 0$). In all the reported studies, the initial fluoride concentration was zero; therefore, the rate inhibition predicted with increasing fluoride concentration by either eq 19a or 19b would not and could not have been observed. Note that eqs 16a and 16b represent distinct pathways and cannot both be correct, so that a resulting differential rate expression would be expressible as eq 19a or 19b, respectively, but not both.

At this point, it is important to point out the distinction between steps that are simultaneous and steps that are kinetically indistinguishable because they occur after the rate-limiting step. For example, eq 17 is not meant to represent a process in which the products are fluoride and silicic acid. Equation 17 is an elementary step, but it is followed by a combination of fast reactions that either have not been or cannot be monitored and do not influence the net reaction rate because they are all faster than the preceding step which governs the rate. It is unreasonable to assume that water substitution in $SiF_4(aq)$ or loss of fluoride from $SiF_4(H_2O)_2$—whatever the case may be—proceeds in one fell swoop. Rather, the most likely scenario is one in which individual fluoride ligands are displaced by either water or hydroxide. It is commonplace to ignore the elementary steps that come after the rate-limiting steps and to write them instead as one subsequent summation reaction. Oftentimes, such elementary steps cannot be discerned. However, such summation reactions should not be interpreted as representing concerted multimolecular processes in which multiple substitutions occur simultaneously. Presumably, the fluoride anions are replaced one at a time through a series of associative or dissociative substitution mechanisms.

To fully explore this system, it would be necessary to fix the initial fluoride concentration at several values to determine whether the rate is invariant to fluoride concentration. There has been no systematic study of the effect of fluoride concentration on the rate, so that any predictions are almost entirely speculative. There is one report of fluoride suppression of the dissociation−hydrolysis, but the results were qualitative and cannot be used to support the existence of a preequilibrium or a rapid reversible reaction that produces a steady-state intermediate.[123]

$$SiF_6^{2-}(aq) \overset{K_1}{\rightleftharpoons} SiF_5^{-}(aq) + F^{-}(aq) \quad (16a)$$

$$SiF_6^{2-}(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SiF_5^{-}(aq) + F^{-}(aq) \quad (16b)$$

$$SiF_5^{-}(aq) + H_2O(l) \xrightarrow{k_2} \text{products} \quad (17)$$

$$-d[SiF_6^{2-}]/dt = k_2[SiF_5^{-}] \quad (18)$$

$$-d[SiF_6^{2-}]/dt = K_1k_2[SiF_6^{2-}]/[F^{-}] \quad (19a)$$

$$-d[SiF_6^{2-}]/dt = \frac{k_1[SiF_6^{2-}]}{\frac{k_{-1}}{k_2}[F^{-}] + 1} \quad (19b)$$

If eq 14 (irreversible as written) is in fact the rate-limiting step in the net dissociation−hydrolysis (eq 4), we would expect it to also be the rate-limiting step for the fluoride exchange reaction (eq 20). Consequently, a comparison of the two reaction rates should be instructive. If eq 16a or 16b is shown to be valid as the first step of the mechanism in the fluoride exchange reaction, then the same initial step can be assumed for the dissociation−hydrolysis. In both reactions, a loss of fluoride must start the process. Whether or not that step is the rate-determining step is of course merely speculative at the present time.

In many ways, the fluoride exchange is more easily studied; its rate of exchange is given by the McKay equation (eq 21).[125] ^{19}F NMR spectrometric studies have shown that the rate (eq 21) of the fluoride exchange is rapid but less than 1000 s^{-1}; both specific and general (Mg^{2+}) acid catalyses were postulated.[44,66] An investigation of the exchange rate using radioactive fluorine ($H^{18}F$) showed that the radiolabel was rapidly distributed between the HF and the SiF_6^{2-}.[126]

$$SiF_6^{2-}(aq) + \underline{F}^{-}(aq) \rightleftharpoons \underline{F}SiF_5^{2-}(aq) + F^{-}(aq);\ \underline{F}^{-} = \text{isotopic label} \quad (20)$$

$$R_{ex} = -\frac{6[SiF_6^{2-}][\underline{F}^{-}]}{[SiF_6^{2-}] + [\underline{F}^{-}]}\cdot\frac{\ln(1-f)}{t};\quad f = \text{fraction of exchange} \quad (21)$$

A catalytic mechanism (eqs 22 and 23) has been put forth for the acceleration of eq 16.[44] It is consistent with the general acid catalysis of dissociation−hydrolysis that was later observed with other Lewis acids, such as Li^+ or Ca^{2+}.[127]

$$H^{+} + SiF_6^{2-} \rightleftharpoons [H{-}F{-}SiF_5^{-}]^{\ddagger} \rightleftharpoons HF + SiF_5^{-} \quad (22)$$

$$SiF_5^{-} + \underline{F}^{-} \rightleftharpoons \underline{F}SiF_5^{2-} \quad (23)$$

It appears that either a metal cation or a proton can help a fluoride ligand off the silicon(IV) center;

CaF^+, LiF, and HF are better leaving groups than F^-. Whether such Lewis acid assistance represents a true dative bond or a weaker ion-pairing association is a matter of debate and does not affect the ability to determine an empirical rate law. The following differential rate expression was reported for the dissociation–hydrolysis of hexafluorosilicate[127]

$$\text{rate} = (k_0 + k_{Li}[Li^+] + k_{Ca}[Ca^{2+}])\,[SiF_6{}^{2-}] \quad (24)$$

where $k_0 = 0.13\ s^{-1}$, $k_{Li} = 0.065\ M^{-1}\ s^{-1}$, and $k_{Ca} = 6.0\ M^{-1}\ s^{-1}$. Equation 24 does not account for specific acid catalysis, and Plakhotnik did not attempt to assess it. It is unclear whether his k_0 included an effect from hydrogen ion or if the possibility of catalysis from hydrogen ion was even considered. Plakhotnik did argue in favor of complexes of the form $[Li-F-SiF_5]^-$,[128] analogous to the proton assistance in eq 22.

The fluoride anion exchange in $SiF_5{}^-$ has been been studied by ^{19}F NMR spectrometry.[129] It has been concluded that the fluoride exchange in pentafluorosilicate is catalyzed by water, based on the loss of coupling with ^{29}Si above −60 °C. Anhydrous $SiF_5{}^-$ appears to undergo Berry pseudorotation (intramolecular exchange), which results in equivalent ^{19}F NMR signals (given the time scale) but not loss of coupling. Addition of nitrogenous bases produced nonequivalent fluoride NMR signals and again no loss in coupling, but the coupling was lost when water was added to the sample and displaced the amine. In dichloromethane, there was rapid interconversion between pentacoordinate $SiF_5{}^-$ and hexacoordinate $SiF_5(H_2O)^-$.

In addition, it was suggested that any Lewis base might catalyze the process. Moreover, it was proposed that $SiF_5{}^-$ decomposition should begin with two rapid equilibria. In the first case (eq 25), there is intermolecular exchange; once the fluoride is removed as HF, any other fluoride is free to recombine.

$$SiF_5{}^- + H_2O \rightleftharpoons SiF_4(OH)^- + HF \quad (25)$$

In the second case (eq 26), there is intramolecular exchange. The trigonal bypyramidal pentafluorosilicate accepts a water ligand to become a pseudooctahedral aquo complex. When the hexacoordinate adduct loses that water molecule, the fluoride ligands assume different orientations than they had in the original trigonal bipyramidal geometry. This experimental fact was determined by varying the temperature and studying the reaction rate in the presence and absence of water.

$$SiF_5{}^- + H_2O \rightleftharpoons SiF_5(H_2O)^- \quad (26)$$

As these results were obtained in a nonaqueous solvent, they suggest that a pentafluorosilicate anion is most likely to be hexacoordinate in an aqueous system, i.e., possess one aquo ligand. Regardless, the process was quite rapid. Note that this study did not address the initial loss of a fluoride from the hexafluorosilicate anion, $SiF_6{}^{2-}$, or the fluoride exchange rate for that species.

Plakhotnik's work is perhaps the most reliable value for the uncatalyzed rate constant. Otherwise, only four studies focused on the kinetics of the dissociation–hydrolysis reaction appear in the literature. Two were performed in the early 20th century.[130,131] The third was published in 1962.[93] The fourth was published in 1975.[94] As these papers are routinely cited as the sources of information of the rate of eq 4, it is beneficial to critically examine them in detail.

In 1921, Hudleston and Bassett made an accidental discovery that "analytical reagent" hydrofluoric acid was contaminated with a considerable concentration of fluorosilicate species.[130] They reported that a fraction of the H^+ was "bound in a complex", and released slowly. They showed this by adding fixed amounts of NaOH and tracking the time until the phenolphthalein was rendered colorless. In their studies, Hudleston and Bassett did not distinguish between the two acid hydrogens of H_2SiF_6 and the six protons produced by subsequent hydrolysis: four from HF and two from $Si(OH)_4$. In failing to distinguish between native H^+ and latent H^+, they hopelessly convolved the rate of the fluorosilicate hydrolysis as explained below. To understand how the data analysis is flawed, it is necessary to understand the experimental procedure in some detail. In the first part of their investigation, Hudleston and Bassett began with fixed volumes of an ill-defined fluorosilicic acid solution (containing fluoride, acid, and fluorosilicates in unknown ratios). This portion of the work was intended to demonstrate the presence of latent hydrogen ions, which was in fact done.

In part two, they used a reagent prepared by the addition of silicon tetrafluoride gas to a suspension of precipitated hydrous silica. The resulting conglomeration shall be represented here as $H_aX(H_b)$, where the native acid hydrogens, H_a, are distinguished from the latent hydrogen ions (H_b) produced by hydrolysis. They titrated all of the hydrogen ions with standard NaOH to a phenolphthalein end point and called this titer N; for clarity, their symbol is replaced here with V_∞. V_∞ represents the total equivalents of H^+ from both acid hydrogen ions and latent hydrogen ions. Next, they added volumes less than V_∞, and timed how long it took until all the NaOH was neutralized based on the loss of the phenolphthalein color. They called these n; their symbol is replaced here with V_t. V_t represents some portion of the total acid, regardless of source. Then they computed a ratio: $C = (V_\infty - V_t)/V_\infty$ = fraction of titratable acid remaining. Finally, they plotted log C against time and reported that a straight line could be drawn through the points.

They believed C represented $[H_aX(H_b)]_t/[H_aX(H_b)]_0$, that is, the ratio of the concentration of the reactant at time t to that at time zero. Consequently, they also believed their plot was equivalent to that for any first-order reaction where $[A]_t/[A]_0 = ([P]_\infty - [P]_t)/([P]_\infty - [P]_0) = \exp(-kt)$ for a reactant A and product P. Their first problem is that they failed to account for $[P]_0$, which was from the acid hydrogens, in other words, they assumed $V_0 = 0$, but—in actuality—$V_0 = 2n_{H_2SiF_6}$. It is rather surprising that the data were able to be fitted to a linear function since the data analysis relied on the erroneous assumption that the acid was all the result of the hydrolysis reaction. However, the acid hydrogen ions are neutralized essentially immediately while the latent hydrogen ions are neutralized slowly. Thus, the kinetic data incorrectly include all of the acid hydrogens of every $\mathrm{H_2SiF_6}$ molecule so that

$$V_t \cdot M_{\mathrm{NaOH}} = 2n_{\mathrm{H_2}}\mathrm{SiF_6} + f \cdot n_{\mathrm{Na_2}}\mathrm{SiF_6} \tag{27}$$

where M_{NaOH} is the molarity of the NaOH solution and f is some fraction of the latent $\mathrm{H^+}$ resulting from the hydrolysis of $\mathrm{Na_2SiF_6}$ to HF and $\mathrm{Si(OH)_4}$.

Their second problem results from the acidity of the silicic acid formed as a product. For a phenolphthalein titration, it is expected that the first acid hydrogen of silicic acid would be at least partly titratable since $\mathrm{p}K_{\mathrm{a1}} = 9.83$[99] and $\mathrm{p}K_{\mathrm{In}} = 9.6$.[132] Since $\mathrm{p}K_{\mathrm{a2}} = 13.17$ for silicic acid, the second proton is probably not titratable using a phenolphthalein end point. From the basic chemical reaction, we know the total stoichiometry between hexafluorosilicic acid (native acid hydrogen ions + latent hydrogen ions) and sodium hydroxide must fall into a range (eq 26). This range is influenced by the titration error associated with the partial neutralization of the silicic acid formed by hydrolysis. Potentiometric titrations support setting $V_\infty \cdot M_{\mathrm{NaOH}} = 6$,[123] but the pH was about 7.0 at the single inflection point observed for the equivalent point. Since equivalence occurs ∼2.6 log units below the $\mathrm{p}K_{\mathrm{a}}$ of phenolphthalein, Hudleston and Bassett's work had to partially titrate the silicic acid, which has one readily accessible deprotonation. It is worth pointing out that the acidity of silicic acid was not well-known at the time, and the equilibrium constants would not be determined until the late 20th century. On the basis of the relationships asserted in eqs 27 and 28, Hudleston and Bassett's C is expressible as eq 29.

$$6n_{\mathrm{H_2}}\mathrm{SiF_6} \le V_\infty \cdot M_{\mathrm{NaOH}} \le 8n_{\mathrm{H_2}}\mathrm{SiF_6} \tag{28}$$

$$C = \frac{An_{\mathrm{H_2SiF_6}} - (2n_{\mathrm{H_2SiF6}} + f \cdot n_{\mathrm{Na_2SiF_6}})}{8n_{\mathrm{H_2SiF6}}} \tag{29}$$

where $1/2 \le A \le 3/4$. Because all of the acid hydrogens must have been neutralized first, $n_{\mathrm{Na_2SiF_6}} = n_{\mathrm{H_2SiF_6}}$; therefore, we can substitute into eq 29 and simplify to obtain

$$C = A - f = A - \Delta n_{\mathrm{Na_2SiF_6}}/n_{\mathrm{Na_2SiF_6}} \tag{30}$$

$$1/2 - \Delta n_{\mathrm{Na_2SiF_6}}/n_{\mathrm{Na_2SiF_6}} \le C \le 3/4 - \Delta n_{\mathrm{Na_2SiF_6}}/n_{\mathrm{Na_2SiF_6}} \tag{31}$$

where $f = \Delta n_{\mathrm{Na_2SiF_6}}/n_{\mathrm{Na_2SiF_6}}$ is the fraction of fluorosilicate consumed and the value of A ranges from 1/2 to 3/4. Because $C \neq [\mathrm{SiF_6}^{2-}]_t/[\mathrm{SiF_6}^{2-}]_0$, it is improper to plot ln C against time.

The third problem is a complication that the authors would not have been aware of at the time of their experiments but nevertheless adversely affects their conclusions. Ideally, there would have been a well-defined mathematical relationship between $[\mathrm{SiF_6}^{2-}]_t/[\mathrm{SiF_6}^{2-}]_0$ and C, and it should have been possible to reanalyze the data, correcting for the stoichiometry problems above. However, the authors reported that they exposed their solutions to precipitated silica for 24 h and allowed silica to dissolve to equilibrium. It has been well-known that additional silicon(IV) is solubilized to give the dimeric species $\mathrm{H_2Si_2F_{10}}$ (vide supra).[52,55,56,102,103] Other polymeric anions, such as $\mathrm{Si_3F_{16}}^{4-}$ have also been speculated and debated.[77,104] Unfortunately, the first of these reports was not until some 20 years after these two investigations were completed. Accordingly, the stoichiometric relationship posited by eq 32 cannot be used to reanalyze the data as the composition of the starting reactant is entirely unknown and most likely includes some combination of dimeric and monomeric silicon(IV) species as well as possibly some HF or NaF as impurities. Under some conditions, even trimeric species may form.[75,76]

As a final point, the use of the term *normality* appears to have been inconsistent, if not incorrect, in some cases. Sometimes "acid normality" seems to refer only to acid hydrogen ions, but other times it seems to refer to the sum of acid and latent hydrogen ions. In some cases, the hydroxide should have been entirely consumed by the acid hydrogens and yet a color change is reported, thereby indicating that the base was in excess shortly after its addition. Such ambiguous (and perhaps even wrong) usage precludes a reanalysis of the data. Overall, such problems are sufficient to discredit the quantitative—but not the qualitative—results thus obtained.

The second study, by Hudleston and Rees in 1936, used similar methods, other than the generation of $\mathrm{SiF_4}$; therefore, it suffers from the same deficiencies. While the summary states that the hydrolysis of $\mathrm{SiF_4}$(aq) produced by the initial dissociation is fast, it looks as though the reaction was not studied independently of the dissociation (as by transferring gaseous $\mathrm{SiF_4}$ to an aqueous solution), and no data for that specific reaction are offered to support the assertion. The only recent studies of $\mathrm{SiF_4}$ hydrolysis have been in the gas phase where silicon tetrafluoride reacts rapidly with excess water to give silicon dioxide and hydrogen fluoride.[86] When water is limited, a variety of partial hydrolysis products can be produced, including some μ-oxo species, such as $\mathrm{(F_3Si)_2O}$ and $\mathrm{(F_3SiO)_2SiF_2}$.

In their 1962 study, Cooke and Minski were careful to begin with $\mathrm{Na_2SiF_6}$ rather than $\mathrm{H_2SiF_6}$, so that did not suffer the problem of the acid hydrogens.[93] Because they used an almost identical experimental technique to Hudleston, Rees, and Bassett,[130,131] the problem of partially titrating silicic acid remains. That notwithstanding, their first order (base 10) plots are demonstrably linear with equal slopes, which increases the confidence in the final result. Their data suggest a half-life of about 110 s (first-order rate constant of 0.0063 $\mathrm{s^{-1}}$), so that the reaction is essentially complete (>99.2% after $7t_{1/2}$) in about 13 min. In all cases, they began with solutions of sodium hexafluorosilicate; therefore, they did not assess possible fluoride, acid, or base dependence. Their starting concentrations ranged from 0.5 to 11 mM, so that any fluoride inhibition, which could have occurred as the reaction proceeded, was probably not observable. The first-order rate constant is substantially different from Plakhotnik's (vide supra), which was 0.13 s^{-1} ($7t_{1/2} = 37$ s). If the true value is near either of these extremes or somewhere between, the reaction is essentially over before the water reaches the consumer. Incomplete understanding of the reaction system, including its intermediates and multiple equilibrium constants, has precluded a thorough investigation of the kinetics. It appears that the studies of the kinetics and the equilibria go hand-in-hand, so that an investigation of one is almost meaningless without accounting for the other.

Westendorf concluded that the dissociation–hydrolysis was completed in 15 min, but his study was complicated by the presence of Mg^{2+} and Ca^{2+}, the effects of which were not taken into account.[94] While this is roughly the same as the results obtained by Cooke and Minski, the equilibrium position was also likely affected by a drop in pH (vide supra). It is uncertain how much weight should be given to this particular result as it was a small part of an overall investigation on biochemical impacts of fluoride at the cellular and molecular level.

V. Conclusions and Unresolved Issues

There is considerable debate over the composition and even the existence of some homo- and heteroleptic aquo-, fluoro-, and hydroxo complexes of silicon(IV), which makes it impossible to predict what species might be found in real potable water supplies that are fluoridated or those that naturally contain fluoride and silicates as background ions. The only agreement seems to be that hexafluorosilicate does not undergo cumulative, consecutive displacements of hydroxide for fluoride. Even this agreed-upon "fact" would seem to be drawn into question by some of the observations of partial hydrolysis products in moist air, suggesting instead that the analytical tools were (are?) incapable of detecting the very low concentrations that might exist. Given the disparity in the speciation models, there is hardly conclusive evidence that consecutive, cumulative substitutions of hydroxide for fluoride are impossible. This assertion is based on the inability to fit potentiometric and some spectrometric data to a suitable system of equations, although it appears to be supported by multiple investigations. The available evidence suggests that neither hexafluorosilicate nor its partial dissociation/hydrolysis products would complex with any transition-metal cations.

Many of the studies of the transformation of hexafluorosilicate have been geared toward ensuring a minimal concentration of free fluoride as a public health measure rather than knowing the equilibrium concentrations of all fluorosilicon(IV) complexes. Whether residual fluorosilicates or fluorosilicon(IV) complexes will be detectable with current instrumentation is debatable. Accounting for the effects of other chemicals on the fluoride speciation will make such analyses even more difficult. Fluoro complexes of some metals are well-studied, but only homoleptic complexes rather than various heteroleptic species that might be encountered in a typical aquatic system where a range of background mineral salts abound. Accordingly, there is a need for further study of heteroleptic fluoride complexes (especially with the common anions in drinking water) of aluminum(III) and possibly other metal cations. However, such research can reasonably be restricted to using fluoride salts (e.g., NaF or KF) rather than fluorosilicates.

Perturbation by dilution (as in a concentration-jump type of experiment) will probably be necessary to understand whether industrial-grade hexafluorosilicic acid actually contains polymers such as $H_2Si_2F_{10}$ which must also undergo reaction when used as drinking water additives. Such approaches may also dispel unsupported claims that heteroleptic species such as $SiF_4(H_2O)_2$ can spontaneously decompose to give $Si(OH)_4$ and SiF_6^{2-}, akin to a disproportionation in redox chemistry.[133]

The kinetics of the dissociation and hydrolysis of hexafluorosilicate are poorly understood from a mechanistic or fundamental perspective. Most of the studies have been rather crude, simply adding a certain amount of the material to water and waiting a set time. The analytical tools applied have not necessarily been chosen for their optimal performance on such a task. The stability of silicon tetrafluoride in water, the formation of aquo (or other) adducts, and the rate of SiF_4 hydrolysis have been studied in a very cursory fashion and barely at all by adding tetrafluorosilane gas to water. Possible inhibitory effects from fluoride have not been investigated; only one qualitative report exists in the literature. Accelerative effects expected from various metal cations or hydrogen ion have not been fully probed.

On the other hand, all the rate data suggest that equilibrium should have been achieved by the time the water reaches the consumer's tap if not by the time it leaves the waterworks plant. Thus, better knowledge of the conditions at equilibrium are critical for planning any pharmacokinetic, pharmacological, toxicokinetic, or toxicological experiments. The EPA is aware of papers positing links between fluoridation agents and lead in the bloodstream or challenging the accepted chemistry.[117,134,135] To truly investigate such hypotheses, better chemical knowledge of the speciation is required. For the time being, it is probably best to stop using qualified expressions such as "virtually complete" or "essentially complete" in favor of more rigorous and quantitative descriptions, even if that hinders communication with the lay public. Once the equilibrium speciation and the rate laws have been better elucidated, it may be possible to perform tests to define a level of *completeness* and the time required to attain that level based on health effects data, which would appear to be most suited to the public health objectives behind drinking water regulation. A purely chemical definition of *complete* would appear to be rather arbitrary in nature, albeit easier to specify.

By definition, the true equilibrium position is not influenced by the direction of approach. In other words, allowing hexafluorosilicate to dissociate and hydrolyze gives the same result as combining fluoride and (hydr)oxosilicates. Nevertheless, it is possible to view the net dissociation−hydrolysis as two distinct phases: a dissociation to SiF_4 and hydrolysis of SiF_4. After all, tetrafluorosilane is a commercially available gas. Of course, it is not necessarily the same as the aquated species (more on that below). That notwithstanding, it is possible for a quasi-equilibrium or pseudo-equilibrium to be observed if the kinetics are influencing product formation. Therefore, it would be ideal to have equilibrium studies conducted from both directions to ensure that previous investigations were not confounded by the formation of semistable intermediates which would make the system biphasic. It is questionable whether the kinetics influence the formation and distribution of observable products, depending on the direction from which equilibrium is approached, namely, diluting a hexafluorosilicate solution as opposed to mixing solutions of fluoride and silicate. In the case of the latter, the existence of polymeric silicate anions may influence the speciation, at least initially.

Because of the forcing and hazardous conditions under which such complexes form and can be studied, it is likely that a mixture of Raman scattering spectroscopy, attenuated total reflectance or mirrored internal reflectance Fourier transform infrared (ATR-FTIR or MIR−FTIR) spectroscopy, and ^{19}F NMR (and ^{29}Si NMR[136]) spectroscopy will be required to study the kinetics and equilibria (using specialized polymer or wax vessels). Like NMR spectroscopy, radioisotope studies may also be used to probe the rate of the fluoride exchange reaction to rule out or verify mechanistic steps. An important factor will be the definitive identification of the composition of the species in equilibrium, so that potentiometric data may be modeled to species already known to exist. In this way, it may be possible to rule out combinations of simultaneous equilibria that are inconsistent with the spectroscopic data even if they provide a satisfactory fit to the potentiometric data. Time resolution may present a problem for NMR, Raman, and IR spectroscopy in that acquisition times necessary for measurement may exceed the duration of the reaction. Chromatographic and electrophoretic techniques will probably be inapplicable to a system that continually shifts to maintain equilibrium unless the separation can be carried out on a time scale during which reequilibration cannot occur. It is not clear if current analytical techniques are capable of detecting whatever species exist under actual drinking water conditions, and such knowledge is critical for the formulation of sound policy and regulation. Table 6 lists species that may exist in fluoridated water systems (regardless of the fluoridating agent owing to natural silica). Ideally, we would like to be able to measure—or at least calculate—the concentrations of those species that do exist and rule out those that do not. Accomplishing this will be no small task, especially when the conditions needed to force a particular species to predominate remain largely unknown. At best, the various equilibrium speciation models reviewed here can collectively serve as a guide. When metal cations are thrown into the mix (as would be the case in a real drinking water matrix), the problem becomes even more difficult.

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

coordination number of the Si^{IV} center	fluorosilicates	aquo/hydroxo /oxosilicates	aquo/hydroxo/ oxo/fluorosilicates
6	SiF_6^{2-} $HSiF_6^-$	$Si(OH)_4(H_2O)_2$	$SiF_5(H_2O)^-$ $SiF_5(OH)^{2-}$ $SiF_4(OH)_2^{2-}$ $SiF_4(H_2O)_2$ $SiF(OH)_2(H_2O)_3^+$
5	SiF_5^- $HSiF_5$	$Si(OH)_5^-$	$SiF_4(OH)^-$
4	SiF_4	$Si(OH)_4$ $SiO(OH)_3^-$ $SiO_2(OH)_2^{2-}$	$SiF_3(OH)$ $SiF_2(OH)_2$ $SiF(OH)_3$
3	none	$SiO(OH)_2$ $SiO_2(OH)^-$	$Si(OH)_2F^+$

In the absence of precise and accurate values for equilibrium constants and well-defined aqueous-phase speciation, another approach might be to obtain reliable values for thermochemical parameters (ΔH_f, ΔG_f, etc.) of individual species. These could then be used to calculate equilibrium constants for reactions otherwise unamenable to current techniques. It seems likely that a mixture of computational and analytical strategies will be required to sort out the exact speciation if such a task is even possible. In the meantime, we must try to make the best use of the information available to us and focus on the consistencies as well as what is unequivocally established as chemical fact.

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