CHEMISTRY AND BIOAVAILABILITY ASPECTS OF FLUORIDE IN DRINKING WATER

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Authors: P J Jackson, P W Harvey and W F Young

Contract Manager: M Hosford

Contract No.: 09607-7

Any enquiries relating to this report should be referred to the authors at the following address:

WRc-NSF Ltd, Henley Road, Medmenham, Marlow, Bucks, SL7 2HD.
Telephone: + 44 (0) 1491 636500   Fax: + 44 (0) 1491 636501

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I   BENEFITS

This report will assist in understanding the chemistry of water fluoridation, possible interactions between fluoride and other chemical species in water, and any effects on bioavailability.

II   OBJECTIVES

The objectives of this report are to answer the following questions:

1. Are there differences in bioavailability of fluoride naturally present and that added to the water supply?

2. Does the presence of different cations in solution in water, and particularly water hardness, affect the bioavailability of fluoride in the gut?

3. In turn, does fluoride (at around 1 mg/l) affect the bioavailability of other constituents of water e.g. aluminium?

4. Does fluoride (at around 1 mg/l) affect the likelihood of interactions either between the constituents of water, or between water and the pipes through with it travels between fluoride dosing at the water treatment works, and the customer's tap?

5. Do other components of the "added fluoride" increase the potential toxicity of the water?

III   REASONS

This project was undertaken to provide an authoritative independent review of the chemical speciation and bioavailability of fluoride in drinking water.

IV   CONCLUSIONS

- Hexafluorosilicate added to fluoridate water is effectively 100% dissociated to form fluoride ion under water treatment conditions. In terms of chemistry and bioavailability there is absolutely no difference between added and "natural" fluoride.

- The effect of major cations – calcium and magnesium (hardness) and sodium – on the chemical speciation and hence bioavailability of fluoride is very small.

- Fluoride forms strong complexes with aluminium so effects on bioavailability are possible. Animal studies suggest that the presence of fluoride may increase the bioavailability of aluminium and that aluminium may decrease the availability of fluoride. However this is based on limited evidence from studies that employed much higher concentrations of aluminium and fluoride than would be present in drinking water.

- The presence of fluoride at a concentration of 1 mg/l will have practically no effect on the chemical speciation and bioavailability of iron, copper or lead.

- Fluoride at a concentration of 1 mg/l will have essentially no interaction with other chemical species in water and negligible impact on corrosivity of water towards the distribution system.

- The quantities of trace metals impurities added as a result of fluoridation are very small and would have no discernible impact on "toxicity" of drinking water.

V   RESUMÉ OF CONTENTS

The approach to chemical speciation modelling is described. <u>Added fluoride is shown to be identical to "natural" fluoride</u>. The effects of calcium and magnesium (water hardness) and sodium on fluoride speciation are calculated. Possible interactions with the trace metals aluminium, iron, copper and lead are modelled. Interactions with other chemical species and the distribution system are considered. The quantities of trace metals added with fluoridation chemicals are calculated both for the minimum specification (worst case) and actual quality of fluoridation chemical.

1. INTRODUCTION

1.1 Background

Fluoridation of drinking water has been practised in various parts of the world for about fifty years but it has become a controversial issue. A recent systematic review by the University of York Centre for Reviews and Dissemination concluded that water fluoridation is effective in reducing tooth decay, and found no evidence of adverse health effects (McDonagh *et al*. 2000). Currently around 10% of the UK population receive fluoridated drinking water. Fluoride is added to achieve a concentration of 1 mg/l as F in drinking water.

This project was undertaken to provide an authoritative independent review of the chemical speciation and bioavailability of fluoride in drinking water.

1.2 Objectives

The objectives of this project are to answer the following questions:

1. Are there differences in bioavailability of fluoride naturally present and that added to the water supply?

2. Does the presence of different cations in solution in water, and particularly water hardness, affect the bioavailability of fluoride in the gut?

3. In turn, does fluoride (at around 1 mg/l) affect the bioavailability of other constituents of water e.g. aluminium?

4. Does fluoride (at around 1 mg/l) affect the likelihood of interactions either between the constituents of water, or between water and the pipes through with it travels between fluoride dosing at the water treatment works, and the customer's tap?

5. Do other components of the "added fluoride" increase the potential toxicity of the water?

Questions 1 to 4 are addressed by modelling the chemical effects and interpreting the chemical speciation data in terms of bioavailability. Question 5 is addressed by considering the impurities that would be added based on specifications and actual product quality data for fluoridation chemicals.

1.3 Approach and terminology

The chemical speciation of fluoride and other water constituents was calculated using chemical equilibrium and mass balance modelling, as detailed in subsequent sections. The influence on bioavailability was then assessed based upon the speciation data.

To keep the chemical models simple and to make the results easier to understand, separate models were constructed to address each question. Clearly, in a real drinking water there are several metals potentially competing for fluoride, and several anions (chloride, sulfate etc.)

competing for metals. It is possible to model this ("fractional speciation modelling") but the results for each individual substance would be less clear-cut.

Throughout this report, square brackets are used to express concentrations in mol/l, e.g. [X] denotes the molar concentration of X. Where concentrations are expressed in other units (e.g. mg/l) the units are quoted. By convention, the concentrations of water and solids are treated as unity when they appear in equilibrium constant expressions.

In chemical speciation modelling it is possible to introduce activity coefficient corrections[1]. This was considered unnecessary for this project; such corrections would be minor and would not have a substantial impact on the overall results and conclusions.

The basis of the chemical equilibrium and mass balance approach is as follows, where M represents a metal and L represents a ligand (anion). Assume M and L form two complexes with the following equilibria:

$$M^+ + L^- \leftrightarrow ML^0$$

$$M^+ + 2L^- \leftrightarrow ML_2^-$$
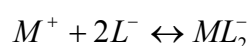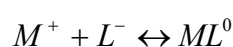
The equilibrium constants are given by:

$$K_1 = \frac{[ML^0]}{[M^+] \times [L^-]} \tag{1}$$

$$K_2 = \frac{[ML_2^-]}{[M^+] \times [L^-]^2} \tag{2}$$

The mass balances are:

$$[M]_T = [M^+] + [ML^0] + [ML_2^-] \tag{3}$$

$$[L]_T = [L^-] + [ML^0] + 2[ML_2^-] \tag{4}$$

where $[M]_T$ and $[L]_T$ are the total concentrations of M and L respectively. If K_1 and K_2 and $[M]_T$ and $[L]_T$ are known the distribution of M and L between the various species can be calculated. The mass balances of Equations 3 and 4, together with Equations 1 and 2, provide four simultaneous equations in the four unknowns. Solution of these equations results in the free ion concentrations from which the complex concentrations can be calculated using Equations 1 and 2. Spreadsheet models were constructed to solve the equilibrium and mass balance equations developed in subsequent sections.

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[1]   In solutions containing ions the effective concentration (or activity) of each ion is depressed by the cloud of other ions surrounding it. The activity is concentration that has been corrected for the non-ideal behaviour in real solutions. The corrections are fairly minor in very dilute solutions such as drinking water (Ionic Strength <0.01 mol/l).

2. ADDED VERSUS "NATURAL" FLUORIDE

All waters contain fluoride at some concentration due to the dissolution of fluoride-containing minerals such as fluorspar (CaF_2). When minerals such as fluorspar dissolve in water they dissociate to produce fluoride ions:

$$CaF_2 \rightarrow Ca^{2+} + 2F^-$$

Fluoridation is carried out using hexafluorosilicic acid (H_2SiF_6) or, far less commonly, sodium hexafluorosilicate (Na_2SiF_6). When hexafluorosilicic acid is dosed into water it hydrolyses releasing fluoride ions (F^-), the <u>overall</u> reaction being:

$$H_2SiF_6 + 4H_2O \leftrightarrow 6F^- + Si(OH)_4 + 6H^+$$
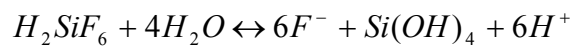
With sodium hexafluorosilicate the reaction is <u>overall</u>:

$$Na_2SiF_6 + 4H_2O \leftrightarrow 6F^- + Si(OH)_4 + 2Na^+ + 4H^+$$
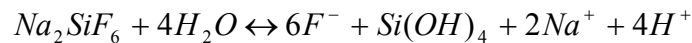
The extent to which the hexafluorosilicate ion, SiF_6^{2-}, dissociates to form fluoride ion (F^-) and silicic acid ($Si(OH)_4$) <u>at equilibrium</u> can be calculated from the hydrolysis constant K_{hyd} for the reaction:

$$SiF_6^{2-} + 4H_2O \leftrightarrow 6F^- + Si(OH)_4 + 4H^+$$
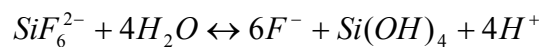
$$K_{hyd} = \frac{[Si(OH)_4] \times [H^+]^4 \times [F^-]^6}{[SiF_6^{2-}]}$$

Rearranging:

$$\frac{[SiF_6^{2-}]}{[Si(OH)_4]} = \frac{[H^+]^4 \times [F^-]^6}{K_{hyd}}$$

Urbansky and Schock (2000) reported that the smallest value of K_{hyd} found in standard reference books is $10^{-31.6}$ – this is the value that would give the lowest calculated dissociation. Using this value and an assumed fluoride ion concentration of 1 mg/l, the amount of undissociated hexafluorosilicate was calculated as a function of pH. The results are given in Table 2.1.

Table 2.1   Undissociated hexafluorosilicate versus pH

pH	$\dfrac{[SiF_6^{2-}]}{[Si(OH)_4]}$
6	$10^{-18.07}$
7	$10^{-22.07}$
8	$10^{-26.07}$
9	$10^{-30.07}$

These results show that the proportion of undissociated hexafluorosilicate is vanishingly small – about 10^{-18} to 10^{-30} of the dissociated hexafluorosilicate – over the range of pH normally encountered in water supply. Note that this calculation was made assuming the lowest ("worst case") value for the hydrolysis constant. It is therefore concluded that, <u>at equilibrium</u>, effectively all of the hexafluorosilicate will have hydrolysed to form free fluoride ion (F^-). The same conclusion would be reached even if the hydrolysis constant used were in error by several orders of magnitude.

Next one needs to consider the rate at which the dissociation reaction proceeds – i.e. to determine whether hexafluorosilicate will fully dissociate to form fluoride ion within the timescale relevant to water treatment and distribution (hours to days). Urbansky and Schock (2000) reviewed the data on hexafluorosilicate dissociation. They concluded that that the mechanism and kinetics have not been adequately investigated but that there is sufficient evidence to suggest that equilibrium is achieved in less than 30 minutes. Based on published experimental data the hydrolysis was calculated to be 99% complete within 12 minutes. It was further noted that other constituents of water, such as calcium, catalyse the reaction making the hydrolysis even faster. Therefore it can be concluded that the hydrolysis of hexafluorosilicate to form fluoride ion is effectively complete by the time the water reaches the consumer's tap.

It is worth noting a practical point. The ion-selective electrode analysers used to monitor and control fluoride dosing at water treatment works respond only to free fluoride ion, not to hexafluorosilicate. They are typically located a few minutes downstream from the hexa-fluorosilicate dosing point. Water undertakers have to make mass balance calculations to satisfy themselves that the quantity of fluoridation chemical dosed over a given period tallies with the measured fluoride ion concentration and volume of water treated. Thus the quantity of fluoride ion detected has to agree with the quantity of hexafluorosilicic acid dosed. This is further evidence that the hydrolysis of hexafluorosilicate is essentially 100% complete under water treatment conditions.

The fluoride ion produced from hexafluorosilicate will behave identically to "natural" fluoride ion present as a result of dissolution of fluoride from minerals. Chemically, and in terms of bioavailability, there is absolutely no difference between added and "natural" fluoride.

3. INTERACTION WITH MAJOR CATIONS

3.1 Equilibria

Stability constants (β) for the formation of complexes with calcium and magnesium have been taken from Nordstrum *et al.* (1990).

$$Ca^{2+} + F^- \leftrightarrow CaF^+ \qquad \beta_{Ca} = \frac{[CaF^+]}{[Ca^{2+}] \times [F^-]} = 10^{0.94}$$

$$Mg^{2+} + F^- \leftrightarrow MgF^+ \qquad \beta_{Mg} = \frac{[MgF^+]}{[Mg^{2+}] \times [F^-]} = 10^{1.82}$$

The concentrations of the complexes, expressed as a proportion of the fluoride ion concentration, are given by:

$$\frac{[CaF^+]}{[F^-]} = \beta_{Ca} \times [Ca^{2+}] \qquad \text{and}$$

$$\frac{[MgF^+]}{[F^-]} = \beta_{Mg} \times [Mg^{2+}]$$

3.2 Mass balance

Considering only fluoride ion and the calcium and magnesium complexes, the total fluoride concentration, $[F]_T$, is given by

$$[F]_T = [F^-] + [CaF^+] + [MgF^+]$$

By substituting the equilibrium expressions and rearranging, the fluoride ion concentration is given by

$$[F^-] = \frac{[F]_T}{1 + \beta_{Ca} \times [Ca^{2+}] + \beta_{Mg} \times [Mg^{2+}]}$$

This equation enables the proportion of free fluoride ion to be calculated as a function of the concentrations of calcium and magnesium. For the purpose of calculation it is assumed that the magnesium concentration, in mg/l as Mg, is equal to 20% of the calcium concentration in mg/l as Ca – a fairly typical ratio.

Hardness of water is commonly expressed in terms of mg/l as $CaCO_3$.

Note: mg/l as $CaCO_3$ = mg/l as Ca $\times$ 2.5

Hardness levels are commonly classified as shown in Table 3.1.

Table 3.1   Classification of water hardness

Description of water	Hardness (mg/l CaCO$_3$)
Soft	up to 50
Moderately soft	50 – 100
Slightly hard	100 – 150
Moderately hard	150 – 200
Hard	200 – 300
Very hard	over 300

The hardness of water supplies in the UK covers a wide range, some examples are given below. It should be noted that these figures are approximate: even within quite small geographical areas there can be large differences in water hardness, and hardness can vary seasonally.

Location	Total hardness mg/l CaCO$_3$ approximate
Glasgow	20
Birmingham	50
Newcastle	120
London	300
Hartlepool	450

Calculations were made for water total hardness over the range 0 to 500 mg/l expressed as CaCO$_3$ which more than covers the range encountered in the UK. The results of the calculations are presented in Figure 3.1.

It can be seen that even with extremely hard waters, 90% or more of the total fluoride is present as free fluoride ion. The amount of calcium and magnesium that would be present as fluoride complexes would be minute – as an example in the presence of 1 mg/l F, <0.05% of the calcium would be present as CaF$^+$.

It can therefore be concluded that the effect of water hardness on the bioavailability of fluoride would be very small.
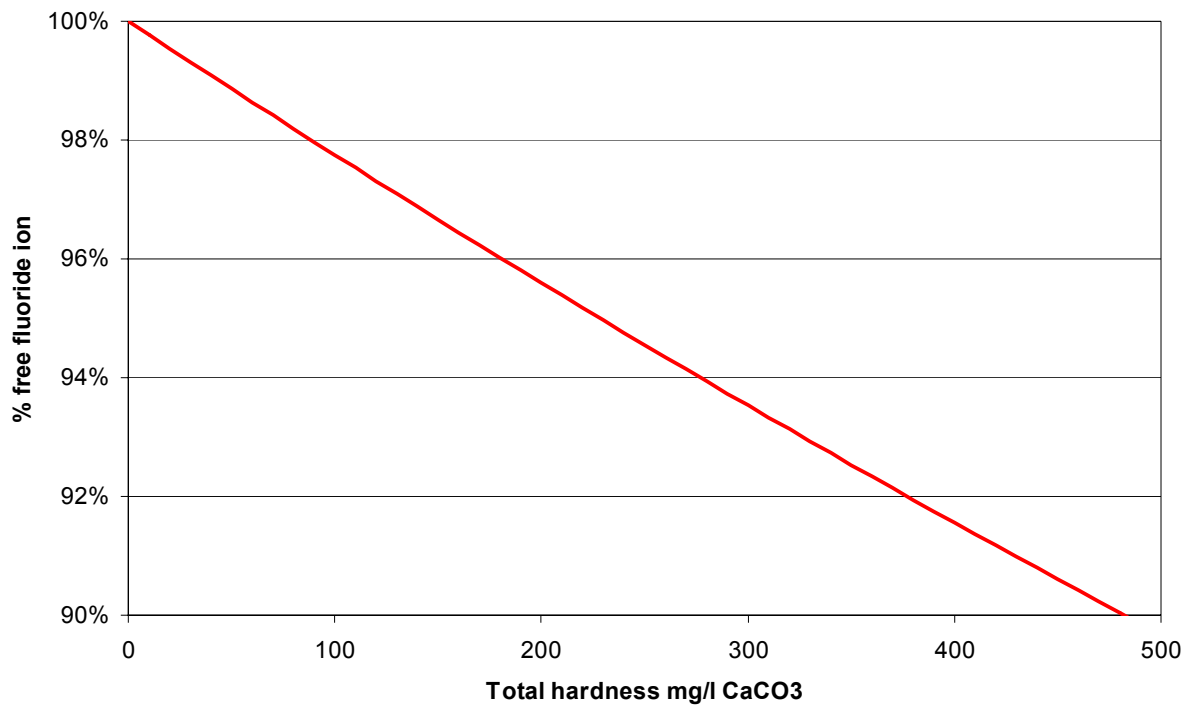
Figure 3.1   Effect of hardness on fluoride ion concentration

Other major cations will have no substantial impact on the concentration of free fluoride ion. Taking sodium as an example:

$$Na^+ + F^- \leftrightarrow NaF \qquad\qquad \beta_{Na} = \frac{[NaF]}{[Na^+] \times [F^-]} = 10^{-0.24}$$

(Nordstrum *et al.* 1990).

By using a similar approach to that for calcium and magnesium, it is calculated that in the presence of 100 mg/l sodium (a relatively high concentration in drinking water) 99.998% of the fluoride would be present as free F⁻.

4. INTERACTION WITH TRACE METALS

4.1 General

The speciation of dissolved trace metals (and fluoride) can be examined in an analogous manner to that described for major cations in Section 3. However, where the concentrations of both metal and fluoride are small and there is a strong interaction between the metal and fluoride, it is necessary to introduce constraints to ensure that the mass balances for both the metal and fluoride are maintained[2]. The approach adopted here is to model the metal speciation using equilibrium constant data and mass balances for the metal and to only impose a mass balance condition for fluoride where a substantial amount of fluoride is calculated to be present as metal-fluoride complexes. Of the metals considered here, this is only necessary in the case of aluminium. Each metal is considered individually. Equilibrium constant data are taken from Nordstrum *et al.* (1990) except where noted.

When modelling interactions of trace metals it is important to choose total trace metal concentrations that are realistic. To do this, and also to provide an estimate of the extent to which fluoride might solubilise metals, the metal solubility and speciation are calculated assuming equilibrium with a metal-containing solid phase that might reasonably be present in suspension or as a deposit in the distribution or plumbing system. It is important to state that this approach, and the choice of solid phase, only affects the calculated solubility and not the calculated proportions of dissolved species.

Hydrogen ion, H^+, and carbonate concentrations are calculated as follows: pH is defined as

$$pH = -\log[H^+]$$

thus

$$[H^+] = 10^{-pH}$$

The equilibrium expressions given later in this report are written such that hydroxide ion, OH^-, does not appear explicitly and it is only necessary to know $[H^+]$.

The alkalinity (ALK) is a capacity factor that represents the acid-neutralising capacity of a water. For waters that contain no protolysis systems other than carbonate the alkalinity is represented by

$$ALK = [HCO_3^-] + 2 \times [CO_3^{2-}] + [OH^-] - [H^+]$$

where ALK and all terms in square brackets are expressed in mol/l.

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad\qquad K = 10^{-10.329}$$

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[2] In the case of calcium and magnesium, the metals mass balances can be neglected because the metals are present in a large excess over fluoride and complexation is weak.

$$K_W = [H^+] \times [OH^-] = 10^{-14}$$

where K_W is the dissociation constant for water. These equations can be combined to express $[CO_3^{2-}]$ in terms of ALK and $[H^+]$:

$$[CO_3^{2-}] = \frac{\left(ALK + [H^+] - \dfrac{K_W}{[H^+]}\right)}{2 + \dfrac{[H^+]}{K}}$$

4.2   <u>Aluminium</u>

Aluminium is naturally present in some waters but arises in drinking water predominantly through the use of aluminium sulfate in the coagulation process of water treatment. The added aluminium precipitates as aluminium hydroxide, removing suspended material and some dissolved substances by adsorption and enmeshment within the precipitate. The precipitated aluminium hydroxide is removed by settlement and filtration. With well-operated plant the residual aluminium concentration passing into supply should not exceed 0.05 mg/l. However, concentrations above this level do occur and aluminium hydroxide can accumulate as a deposit within distribution systems (e.g. in dead ends).

The speciation of aluminium was calculated assuming equilibrium with aluminium hydroxide. Reported values for the solubility product of aluminium hydroxide span a wide range. Here, a value reported for amorphous aluminium hydroxide was taken (Hayden and Rubin 1974).

$$Al(OH)_3(s) + 3H^+ \leftrightarrow Al^{3+} + 3H_2O \qquad\qquad K_{sp} = 10^{10.4}$$
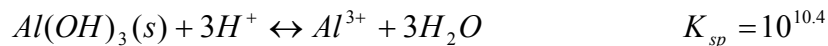
Apart from fluoride complexes, the predominant aluminium species in drinking water are the hydroxide complexes listed in Table 4.1.

The calculations were made using a total available fluoride concentration of 1 mg/l. Because fluoride forms strong complexes with aluminium, the solution of the equations was constrained such that the sum of total dissolved fluoride (free ion plus complexes) was equal to 1 mg/l as F.

The results for aluminium solubility and speciation are given in Table 4.2. This shows the total dissolved aluminium concentration in equilibrium with aluminium hydroxide solid with pH from 6 to 9, together with the distribution of dissolved aluminium species. In this and subsequent tables in this section, speciation results are rounded to the nearest 0.01%. The species AlF_5^{2-} and AlF_6^{3-} are not significant (<0.005% of total).

The fluoride complexes account for a substantial proportion of the dissolved aluminium only at pH values less than 7. At pH 6 in the presence of 1 mg/l total fluoride the calculated solubility of aluminium is 0.649 mg/l compared to 0.083 mg/l in the absence of fluoride – a substantial increase. This indicates that fluoride could solubilise aluminium deposits within distribution, for example. The distribution of the dissolved fluoride species is shown in Table 4.3. Overall the results demonstrate that fluoride forms strong complexes with aluminium.

Table 4.1   Formation constant data for aluminium species

Reaction	β
$Al^{3+} + H_2O \leftrightarrow AlOH^{2+} + H^+$	$10^{-5.0}$
$Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^+ + 2H^+$	$10^{-10.1}$
$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3^0 + 3H^+$	$10^{-16.9}$
$Al^{3+} + 4H_2O \leftrightarrow Al(OH)_4^- + 4H^+$	$10^{-22.7}$
$Al^{3+} + F^- \leftrightarrow AlF^{2+}$	$10^{7.0}$
$Al^{3+} + 2F^- \leftrightarrow AlF_2^+$	$10^{12.7}$
$Al^{3+} + 3F^- \leftrightarrow AlF_3^0$	$10^{16.8}$
$Al^{3+} + 4F^- \leftrightarrow AlF_4^-$	$10^{19.4}$
$Al^{3+} + 5F^- \leftrightarrow AlF_5^{2-}$	$10^{20.6}$
$Al^{3+} + 6F^- \leftrightarrow AlF_6^{3-}$	$10^{20.6}$

Table 4.2   Dissolved aluminium speciation in the presence of 1 mg/l F

pH	Total Al mg/l	Percent of total dissolved aluminium								
		Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$Al(OH)_3^0$	$Al(OH)_4^-$	AlF^{2+}	AlF_2^+	AlF_3^0	AlF_4^-
6	0.65	0.10	1.04	8.29	1.31	2.08	11.73	66.05	9.34	0.04
7	0.16	0.00	0.04	3.27	5.19	82.26	0.21	5.44	3.51	0.07
8	1.36	0.00	0.00	0.04	0.63	99.33	0.00	0.00	0.00	0.00
9	13.53	0.00	0.00	0.00	0.06	99.94	0.00	0.00	0.00	0.00

Table 4.3   Dissolved fluoride speciation in the presence of aluminium

pH	Percent of total dissolved fluoride				
	F^-	AlF^{2+}	AlF_2^+	AlF_3^0	AlF_4^-
6	21.35	5.36	60.40	12.82	0.08
7	97.46	0.02	1.26	1.22	0.03
8	100.00	0.00	0.00	0.00	0.00
9	100.00	0.00	0.00	0.00	0.00

Two studies have been found on bioavailability where aluminium and fluoride were experimentally manipulated in drinking water and concentrations in bones measured – these are reviewed in Appendix A. Both studies used high dose levels and animal models, the rat and rabbit, which may not be the most relevant models for extrapolation to humans because of differences in gastrointestinal systems.

In the study on rats (Wicklund Glynn *et al*. 2001) fluoride alone (50 mg/l) did not affect the concentration of aluminium in the stomach contents of rats given water with 100 mg/l Al. These concentrations of fluoride and aluminium are extremely high in comparison with values that would be present in drinking water. There was a slight increase when silicate (200 mg/l) was also present (silicate would be present if fluorosilicate chemicals were dosed but at much lower concentration). There were only slight, non-significant, changes in Al concentrations in the femur caused by the presence of either or both fluoride and silicate together with aluminium in drinking water. Thus fluoride had no effect on aluminium absorption or bone contents in the rat. Citrate was the only compound that influenced aluminium absorption in this study.

In the study on rabbits (Ahn *et al*. 1995) the presence of aluminium (100 or 500 mg/l) was found to decrease the absorption of fluoride from the gastrointestinal tract. The presence of fluoride increased the absorption of aluminium into bone.

Overall it can not be stated that the presence of fluoride (whether naturally present or artificially adjusted) increases the uptake (bioavailability) of aluminium from drinking water: evidence of an effect was seen in one study in rabbits but there were no effects in rats. The presence of aluminium may decrease the bioavailability of fluoride. There is a need for further confirmatory studies before any conclusions can be drawn on the interaction of fluoride with aluminium and the bioavailability of either element.

4.3   Iron(III)

Iron is naturally present in some waters but arises in drinking water predominantly through the use of iron(III) sulfate in the coagulation process of water treatment. The added iron precipitates as iron(III) hydroxide, removing suspended material and some dissolved substances by adsorption and enmeshment within the precipitate. The precipitated iron(III) hydroxide is removed by settlement and filtration. With well-operated plant the residual iron concentration passing into supply should not exceed 0.05 mg/l. However, concentrations above this level do occur and iron(III) hydroxide can accumulate as a deposit within distribution systems (e.g. in dead ends). Iron can also be found as a consequence of corrosion of cast iron mains.

The speciation of iron was calculated assuming equilibrium with iron(III) hydroxide using the following value[3] for the solubility product.

$$Fe(OH)_3(s) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O \qquad K_{sp} = 10^{6.0}$$

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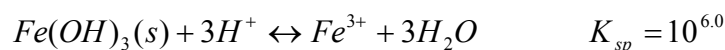
[3] This value was chosen to generate solubilities of the same order as found in practice. Published values generate unrealistically low iron(III) solubility.

The predominant iron(III) species in drinking water are the hydroxide complexes listed in Table 4.4.

The results for iron speciation are given in Table 4.5. Less than 0.005% of the iron(III) is present as fluoride complexes; the presence of fluoride at 1 mg/l has essentially no effect on the solubility of iron. Therefore fluoride will not affect the bioavailability of iron.

Table 4.4   Formation constant data for iron(III) species

Reaction	β
$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+$	$10^{-2.19}$
$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+$	$10^{-5.67}$
$Fe^{3+} + 4H_2O \leftrightarrow Fe(OH)_4^- + 4H^+$	$10^{-21.6}$
$Fe^{3+} + F^- \leftrightarrow FeF^{2+}$	$10^{5.2}$
$Fe^{3+} + 2F^- \leftrightarrow FeF_2^+$	$10^{9.1}$
$Fe^{3+} + 3F^- \leftrightarrow FeF_3^0$	$10^{11.9}$

Table 4.5   Dissolved iron speciation in the presence of 1 mg/l F

pH	Total Fe mg/l	Percent of total dissolved iron						
		Fe^{3+}	$FeOH^{2+}$	$Fe(OH)_2^+$	$Fe(OH)_4^-$	FeF^{2+}	FeF_2^+	FeF_3^0
6	0.120	0.00	0.30	99.69	0.01	0.00	0.00	0.00
7	0.012	0.00	0.03	98.81	1.16	0.00	0.00	0.00
8	0.003	0.00	0.00	45.98	54.02	0.00	0.00	0.00
9	0.014	0.00	0.00	0.84	99.16	0.00	0.00	0.00

4.4   Copper

Copper in drinking water arises mainly from the corrosion of copper pipework in the domestic water distribution system. As corrosion progresses a thin layer of corrosion product (copper compound) is formed inside the pipe. A large number of compounds are potential corrosion products (AWWARF 1996). For the purpose of solubility and speciation modelling, malachite ($Cu_2(OH)_2CO_3$) was taken as the copper solid. The solubility product of malachite is (AWWARF 1996):

$$Cu_2(OH)_2CO_3 + 2H^+ \leftrightarrow 2Cu^{2+} + CO_3^{2-} + 2H_2O \qquad K_{sp} = 10^{-5.16}$$
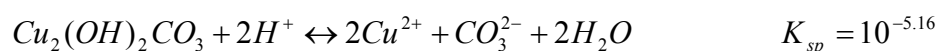
The predominant dissolved copper(II) species in drinking water are the hydroxide and carbonate complexes listed in Table 4.6.

In order to model the concentrations of the carbonate complexes, a range of pH values and alkalinity were used. The results are summarised in Table 4.7.

Table 4.6   Formation constant data for copper(II) species

Reaction	β
$Cu^{2+} + H_2O \leftrightarrow CuOH^+ + H^+$	$10^{-7.97}$
$Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2^0 + 2H^+$	$10^{-16.24}$
$Cu^{2+} + 3H_2O \leftrightarrow Cu(OH)_3^- + 3H^+$	$10^{-26.90}$
$Cu^{2+} + 4H_2O \leftrightarrow Cu(OH)_4^{2-} + 4H^+$	$10^{-39.56}$
$Cu^{2+} + HCO_3^- \leftrightarrow CuHCO_3^+$	$10^{1.80}$
$Cu^{2+} + CO_3^{2-} \leftrightarrow CuCO_3^0$	$10^{6.82}$
$Cu^{2+} + 2CO_3^{2-} \leftrightarrow Cu(CO_3)_2^{2-}$	$10^{10.60}$
$Cu^{2+} + F^- \leftrightarrow CuF^+$	$10^{1.2}$

Under all the conditions examined, the fluoride complex accounts for less than 0.1% of the dissolved copper. The most complexing is predicted to occur at low pH and low alkalinity (pH 6, alkalinity 10 mg/l as $CaCO_3$) but even under these conditions the presence of 1 mg/l fluoride would only increase copper solubility by 0.05%. Therefore fluoride will not affect the bioavailability of copper.

4.5   Lead

Lead in drinking water arises almost exclusively from the corrosion of lead pipework, leaded solders and leaded alloys in the domestic water distribution system. As corrosion progresses a thin layer of corrosion product (lead carbonate) is formed inside the pipe. Of the potential lead carbonates (AWWARF 1996) hydrocerussite ($Pb_3(OH)_2(CO_3)_2$) was taken as the solid. The solubility product of hydrocerussite is (AWWARF 1996):

$$Pb_3(OH)_2(CO_3)_2 + H^+ \leftrightarrow 3Pb^{2+} + 2CO_3^{2-} + 2H_2O \quad K_{sp} = 10^{-18.00}$$
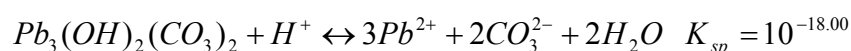
The predominant dissolved lead(II) species in drinking water are the hydroxide and carbonate complexes listed in Table 4.8.

Table 4.7   Dissolved copper speciation in the presence of 1 mg/l F

pH	Alkalinity mg/l CaCO$_3$	Total Cu mg/l	Percent of total dissolved copper								
			Cu^{2+}	$CuOH^+$	$Cu(OH)_2^0$	$Cu(OH)_3^-$	$Cu(OH)_4^{2-}$	$CuHCO_3^+$	$CuCO_3^0$	$Cu(CO_3)_2^{2-}$	CuF^+
6	10	1.828	92.04	0.99	0.01	0.00	0.00	1.17	5.73	0.00	0.08
7	10	0.199	84.97	9.10	0.49	0.00	0.00	0.11	5.26	0.00	0.07
8	10	0.046	36.89	39.53	21.23	0.05	0.00	0.00	2.27	0.00	0.03
9	10	0.122	1.42	15.18	81.53	1.78	0.00	0.00	0.08	0.00	0.00
6	50	1.044	72.21	0.77	0.00	0.00	0.00	4.56	22.39	0.01	0.06
7	50	0.108	69.94	7.49	0.40	0.00	0.00	0.44	21.66	0.01	0.06
8	50	0.022	33.79	36.21	19.45	0.04	0.00	0.02	10.46	0.00	0.03
9	50	0.054	1.41	15.13	81.25	1.78	0.00	0.00	0.43	0.00	0.00
6	100	0.938	56.89	0.61	0.00	0.00	0.00	7.18	35.25	0.02	0.05
7	100	0.093	57.27	6.14	0.33	0.00	0.00	0.72	35.47	0.02	0.05
8	100	0.017	30.58	32.77	17.60	0.04	0.00	0.04	18.93	0.01	0.03
9	100	0.038	1.41	15.06	80.89	1.77	0.00	0.00	0.87	0.00	0.00
6	200	0.945	39.93	0.43	0.00	0.00	0.00	10.08	49.48	0.06	0.03
7	200	0.090	42.03	4.50	0.24	0.00	0.00	1.06	52.07	0.06	0.04
8	200	0.015	25.70	27.53	14.79	0.03	0.00	0.06	31.83	0.04	0.02
9	200	0.027	1.39	14.93	80.19	1.75	0.00	0.00	1.72	0.00	0.00
6	300	1.001	30.75	0.33	0.00	0.00	0.00	11.64	57.15	0.10	0.03
7	300	0.093	33.19	3.56	0.19	0.00	0.00	1.26	61.67	0.10	0.03
8	300	0.014	22.15	23.74	12.75	0.03	0.00	0.08	41.16	0.07	0.02
9	300	0.022	1.38	14.80	79.50	1.74	0.00	0.00	2.56	0.00	0.00

Table 4.8   Formation constant data for lead(II) species

Reaction	β
$Pb^{2+} + H_2O \leftrightarrow PbOH^+ + H^+$	$10^{-7.22}$
$Pb^{2+} + 2H_2O \leftrightarrow Pb(OH)_2^0 + 2H^+$	$10^{-16.91}$
$Pb^{2+} + 3H_2O \leftrightarrow Pb(OH)_3^- + 3H^+$	$10^{-28.08}$
$Pb^{2+} + 4H_2O \leftrightarrow Pb(OH)_4^{2-} + 4H^+$	$10^{-39.72}$
$Pb^{2+} + HCO_3^- \leftrightarrow PbHCO_3^+$	$10^{2.26}$
$Pb^{2+} + CO_3^{2-} \leftrightarrow PbCO_3^0$	$10^{7.10}$
$Pb^{2+} + 2CO_3^{2-} \leftrightarrow Pb(CO_3)_2^{2-}$	$10^{10.33}$
$Pb^{2+} + F^- \leftrightarrow PbF^+$	$10^{2.06}$
$Pb^{2+} + 2F^- \leftrightarrow PbF_2^0$	$10^{3.42}$

In order to model the concentrations of the carbonate complexes, a range of pH values and alkalinity were used. The results are summarised in Table 4.9.

Under all the conditions examined the fluoride complexes accounted for less than 0.5% of the dissolved lead. The most complexing is predicted to occur at low pH and low alkalinity (pH 6, alkalinity 10 mg/l as $CaCO_3$) but even under these conditions the presence of 1 mg/l fluoride would only increase lead solubility by 0.5%. Therefore fluoride will not affect the bioavailability of lead.

In fact, Urbansky and Schock (2000) have considered the possible complexation of lead by fluoride and hexafluorosilicate in great depth. They used a fractional speciation model that considered all likely water constituents and their interactions (i.e. a sophisticated model that considered all species together, rather than constructing separate models as done here). They found that the lead fluoride complexes accounted for less than 1% of the total dissolved lead under the conditions modelled – i.e. essentially the same result as reported above. They included the species $PbSiF_6$ and found that its concentration would be vanishingly small; one molecule in 1000 litres of water at pH 6. They also showed that the small pH drop caused by dosing hexafluorosilicic acid has an insignificant effect on solubilising lead. Overall they concluded that "No credible evidence exists to show that water fluoridation has any quantitatable effects on the solubility, bioavailability, bioaccumulation or reactivity of lead(0) or lead(II) compounds".

Table 4.9   Dissolved lead speciation in the presence of 1 mg/l F

pH	Alkalinity mg/l CaCO$_3$	Total Pb mg/l	Percent of total dissolved lead
			Pb^{2+}	$PbOH^+$	$Pb(OH)_2^0$	$Pb(OH)_3^-$	$Pb(OH)_4^{2-}$	$PbHCO_3^+$	$PbCO_3^0$	$Pb(CO_3)_2^{2-}$	PbF^+	PbF_2^0
6	10	5.646	82.27	4.96	0.00	0.00	0.00	3.01	9.76	0.00	0.00	0.00
7	10	1.732	57.96	34.92	0.07	0.00	0.00	0.21	6.84	0.00	0.00	0.00
8	10	1.577	13.76	82.92	1.69	0.00	0.00	0.00	1.62	0.00	0.00	0.00
9	10	3.557	1.36	81.70	16.68	0.11	0.00	0.00	0.15	0.00	0.00	0.00
6	50	2.920	54.55	3.29	0.00	0.00	0.00	9.94	32.22	0.00	0.00	0.00
7	50	0.760	45.20	27.24	0.06	0.00	0.00	0.82	26.68	0.00	0.00	0.00
8	50	0.573	12.92	77.85	1.59	0.00	0.00	0.02	7.62	0.00	0.00	0.00
9	50	1.191	1.35	81.18	16.57	0.11	0.00	0.00	0.79	0.00	0.00	0.00
6	100	2.615	38.38	2.31	0.00	0.00	0.00	13.97	45.32	0.01	0.00	0.00
7	100	0.610	35.45	21.36	0.04	0.00	0.00	1.29	41.84	0.01	0.00	0.00
8	100	0.388	12.00	72.32	1.48	0.00	0.00	0.04	14.16	0.00	0.00	0.00
9	100	0.754	1.34	80.54	16.44	0.11	0.00	0.00	1.57	0.00	0.00	0.00
6	200	2.624	24.10	1.45	0.00	0.00	0.00	17.54	56.89	0.02	0.00	0.00
7	200	0.550	24.77	14.92	0.03	0.00	0.00	1.80	58.46	0.02	0.00	0.00
8	200	0.279	10.51	63.32	1.29	0.00	0.00	0.08	24.80	0.01	0.00	0.00
9	200	0.481	1.32	79.29	16.19	0.11	0.00	0.00	3.10	0.00	0.00	0.00
6	300	2.749	17.56	1.06	0.00	0.00	0.00	19.17	62.18	0.03	0.00	0.00
7	300	0.547	19.03	11.47	0.02	0.00	0.00	2.08	67.37	0.03	0.00	0.00
8	300	0.240	9.34	56.31	1.15	0.00	0.00	0.10	33.08	0.02	0.00	0.00
9	300	0.373	1.30	78.07	15.94	0.11	0.00	0.00	4.58	0.00	0.00	0.00

5.   INTERACTIONS BETWEEN WATER CONSTITUENTS AND WITH THE DISTRIBUTION SYSTEM

It has been shown in Sections 3 and 4 that, with the notable exception of aluminium, major and minor cations present in water do not react to any significant extent with fluoride. There is no plausible mechanism by which fluoride could react with anions. At the concentrations applied for fluoridation, fluoride ion could not cause significant interactions between other species (e.g. by forming chemical bridges).

There is very little published information on the effects of fluoridation on distribution system corrosion. This is probably because any such effects are negligible and do not cause any problems in practice. Addition of hexafluorosilicic acid will cause a reduction in both pH and alkalinity. However, considering the low dose used in practice, such effects are likely to be negligible except in very soft, poorly buffered, waters. Calculations[4] show, for example, that addition of hexafluorosilicic acid at a dose of 1 mg/l as F would reduce the pH from 7.00 to 6.70 in a soft poorly buffered water (alkalinity 20 mg/l as $CaCO_3$). In harder water (alkalinity 200 mg/l as $CaCO_3$) the pH would only drop to pH 6.96. Sodium hexafluorosilicate will slightly reduce pH and alkalinity. Urbansky and Schock (2000) who modelled the effects on pH and buffer capacity support this conclusion.

In practice, water undertakers add alkali to adjust the pH to an appropriate value before the water is pumped into supply.

Fluoride ion probably enhances corrosion in the same way as chloride and sulfate ions do (AWWARF 1996). However, it seems unlikely that addition of 1 mg/l of fluoride ion would have a noticeable effect on corrosion, considering the background levels of other ions in the water.

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[4] These calculations were made using WaQCoM – a WRc-NSF package for modelling the effects of treatment and blending on water quality and corrosion propensity. The calculation method is similar to that described by Trussell (1998).

6.   IMPURITIES IN FLUORIDATION CHEMICALS

The impact of adding fluoride on trace metals concentrations in drinking water can be determined by considering the specifications for fluoridation chemicals (the "worst case"), and by calculations based upon actual product quality.

The European Committee for Standardization (CEN) is developing harmonised standards (ENs) for water treatment chemicals under European Union legislation. These are published by the British Standards Institution as BS ENs. Water treatment chemicals which conform with a BS EN may be used without the approval of the Authorities, provided that any national conditions of use are observed – in the case of fluoridation chemicals, they have to be used in accordance with the UK Code of Practice (DoE 1987).

European standards for hexafluorosilicic acid and sodium hexafluorosilicic acid have recently been adopted and published by BSI (BS ENs 12174 and 12175). These standards are listed in the latest List of Approved Products (DWI 2001). The standards contain requirements for product purity that are summarised in Tables 6.1 and 6.2.

Table 6.1   European standard BS EN 12175 for hexafluorosilicic acid

Parameter	Units	Value
H_2SiF_6	% *m/m*	spec. ±5
Free acid (HF)	mg/kg product max.	1.5
Phosphate (P_2O_5)	mg/kg product max.	0.75
As	mg/kg H_2SiF_6 max.	400
Cd	mg/kg H_2SiF_6 max.	40
Cr	mg/kg H_2SiF_6 max.	400
Hg	mg/kg H_2SiF_6 max.	10
Ni	mg/kg H_2SiF_6 max.	400
Pb	mg/kg H_2SiF_6 max.	400
Sb	mg/kg H_2SiF_6 max.	80
Se	mg/kg H_2SiF_6 max.	80

Table 6.2   European standard BS EN 12174 for sodium hexafluorosilicate

Parameter	Units	Value
Na_2SiF_6	% *m*/*m* min.	98
Moisture	% *m*/*m* product max.	0.3
Insolubles	% *m*/*m* product max.	0.5
As	mg/kg product max.	400
Cd	mg/kg product max.	40
Cr	mg/kg product max.	400
Hg	mg/kg product max.	10
Ni	mg/kg product max.	400
Pb	mg/kg product max.	400
Sb	mg/kg product max.	80
Se	mg/kg product max.	80

The maximum concentration of a contaminant that could be added to drinking water as a result of adding a particular dose of chemical is given by:

$$C = \frac{L \times D}{1000} \qquad (5)$$

where   *C* is the concentration of contaminant added, μg/l,
L is the limit on the concentration of the impurity in the chemical, mg/kg, and
D is the dose of chemical applied, mg/l.

Using Equation 5, the concentrations of trace metals that would be added, assuming a fluoride dose of 1 mg/l as F and the limit values in the ENs, have been calculated. These are shown in Tables 6.3 and 6.4, with the Parametric Values (PV) specified in the 1998 Drinking Water Directive (EC 1998) for comparison. Even at a dose of 1 mg/l as F, the highest that would be used in practice, only about 5% of the PV for certain parameters could be added by a product that contained the maximum permitted levels of trace metals.

In practice, trace metal contents are lower than the limits in the European standards. The vast majority of fluoridation plants in the UK employ hexafluorosilicic acid as the fluoridating agent. Figure 6.1 shows a summary of data on hexafluorosilicic acid supplied by Hydro Chemicals, based on monthly analyses over the period January 1996 to June 2000[5]. The maximum trace metal concentrations found were approximately 20% of the limit in the European standard (data for selenium were not available). Thus, dosing commercial hexafluorosilicic acid at a rate of 1 mg/l as F will add less than 1% of the maximum permitted levels of trace metals. The permitted limits in drinking water are based on values derived by the World Health Organization as being safe for a lifetime's exposure (consumption of 2 litres of water per day over 70 years).

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[5]   Bob Hassall, Hydro Chemicals (UK) Limited, Personal Communication, June 2000.

Table 6.3   Impurities added by dosing hexafluorosilicic acid

Element	Limit, mg/kg H_2SiF_6	µg/l added at 1 mg/l F dose	Parametric Value in DWD (µg/l)	% of PV added
As	400	0.51	10	5.1
Cd	40	0.05	5	1.0
Cr	400	0.51	50	1.0
Hg	10	0.01	1	1.3
Ni	400	0.51	20	2.5
Pb	400	0.51	10	5.1
Sb	80	0.10	5	2.0
Se	80	0.10	10	1.0

Table 6.4   Impurities added by dosing sodium hexafluorosilicate

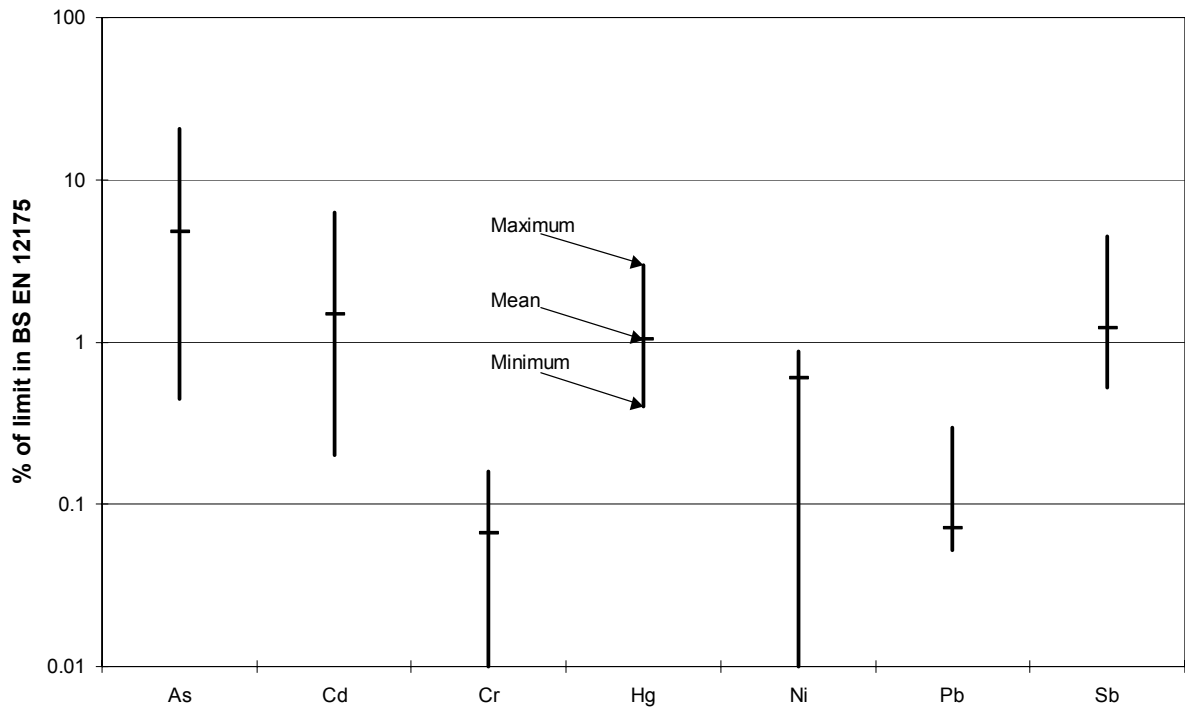| Element	Limit, mg/kg Na_2SiF_6	µg/l added at 1 mg/l F dose	Parametric Value in DWD (µg/l)	% of PV added
As	400	0.67	10	6.7
Cd	40	0.07	5	1.3
Cr	400	0.67	50	1.3
Hg	10	0.02	1	1.7
Ni	400	0.67	20	3.3
Pb	400	0.67	10	6.7
Sb	80	0.13	5	2.7
Se	80	0.13	10	1.3

Figure 6.1   Summary of quality of hexafluorosilicic acid

7.   CONCLUSIONS

1. Hexafluorosilicate added to fluoridate water is effectively 100% dissociated to form fluoride ion under water treatment conditions. Therefore in terms of chemistry and bioavailability there is absolutely no difference between added and "natural" fluoride.

2. The effect of major cations – calcium and magnesium (hardness) and sodium – on the chemical speciation and hence bioavailability of fluoride is very small.

3. Fluoride forms strong complexes with aluminium so effects on bioavailability are possible. Animal studies suggest that the presence of fluoride may increase the bioavailability of aluminium and that aluminium may decrease the availability of fluoride. However this is based on limited evidence from studies that employed much higher concentrations of aluminium and fluoride than would be present in drinking water.

4. The presence of fluoride at a concentration on 1 mg/l will have practically no effect on the chemical speciation and bioavailability of iron, copper or lead.

5. At a concentration of 1 mg/l as F, fluoride could not cause significant interactions between other chemical species in drinking water. Fluoride at a concentration of 1 mg/l will have negligible impact on corrosivity of water towards the distribution system.

6. The quantities of trace metals impurities added as a result of fluoridation are very small and would have no discernible impact on "toxicity" of drinking water.

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APPENDIX A   REVIEW OF FLUORIDE AND ALUMINIUM IN DRINKING WATER STUDIES

A.1   WICKLUND GLYNN, A *ET AL* (2001)

The influence of citrate (0-31 mM), fluoride (0 or 2.6mM) and silicate (0 or 2.6 mM) on the absorption of aluminium (Al; 0-18mM) administered in drinking water was studied in Sprague-Dawley rats to examine whether complexing agents increase Al absorption from the gastrointestinal (GI) tract. Male rats (juveniles, 80-90g in weight) were exposed for 6-7 weeks to soluble Al in acidic drinking water (pH 2.5-3.0, acidified using ratios of sulfuric acid with sodium hydroxide) and Al content in stomach and femur were analysed.

The addition of citrate (6 g/L) to spiked water containing Al (10 or 500 mg/l as Al) increased the concentration of soluble Al in stomach by 1.2 and 2.6 fold respectively compared with concentrations achieved with the Al only groups. However, fluoride (50 mg/l) or silicate (200 mg/l) alone did not affect soluble Al concentrations in stomach contents of rats given water with 100 mg/l Al: a slightly increased gastric content of soluble aluminium was seen in the Al+F+Si group compared with Al alone. It is noted that a large fraction of soluble Al became insoluble after ingestion.

In the femur studies, spiking water with 10 mg/l Al alone did not affect Al concentrations in this bone, however the addition of citrate to water spiked with 10 mg/l Al resulted in increased bone Al concentrations indicating that the addition of citrate increased GI absorption of Al. The addition of 500 mg/l of Al to drinking water increased femur concentrations of Al and the addition of citrate markedly increased bone Al concentrations (5 fold) compared with the Al only group. In the fluoride/silicate experiment, adding 100 mg/l Al to water increased bone concentrations of Al and the addition of fluoride alone, silicate alone or both fluoride+silicate to Al spiked drinking water only produced slight non-significant increments in bone Al concentrations.

The results indicate that the concentration of soluble Al increased only in the presence of citrate or a mixture of fluoride and silicate and citrate was the only complexing agent that influenced absorption in the rat.

A.2   AHN, H-W *ET AL* (1995)

Fluoride (F) and Aluminium (Al) form a strong complex and are both present in drinking water, and this study examines how they affect one another's tissue accumulation in adult (1.4-2.2 kg) male New Zealand white rabbits. Animals were allocated to 12 groups of 3 consisting of control, 1, 4 and 50 mg/l F (as NaF), 100 and 500 mg/l Al (as aluminium chloride) and all combinations of the two- 1 mg/l F+100 mg/l Al (1+100), 4+100, 50+100, 1+500, 4+500 and 50+500. Both F and Al were analysed in plasma, urine, liver, incisors and tibia. Results showed that in plasma, urine and tibia the level of F decreased as the level of aluminium increased and this was particularly marked in the 50 mg/l F group. This indicates that Al decreases F absorption from the gastrointestinal tract. Additionally, Al levels in tibia were increased when F was added to drinking water (this was also confirmed in rats given 79 mg/l NaF in drinking water for 2 years in an NTP study when samples were analysed for Al by Ahn et al). It was concluded that Al decreases F absorption and that F increases Al absorption into bone and that some of the osteotoxicity of F may be due to Al or Al-F complexes.