

Technical and scientific aspects of water fluoridation

KEY POINTS

- **Worldwide there are many thousands of fluoridation schemes in operation – the earliest dating from 1945. Water suppliers have therefore accumulated a wealth of practical experience in managing the fluoridation process safely and efficiently.**
- **The fluoride materials used in water fluoridation schemes are derived from the same minerals in rocks that give rise to naturally occurring fluoride in water that passes over the rocks.**
- **The fluoride ion produced from artificial fluoridation behaves identically to the fluoride ion naturally present in water supplies. It means that, chemically, there is no difference between artificial and natural fluoridation.**
- **In the UK, the fluoridation process is governed by a detailed code of practice issued by the Drinking Water Inspectorate (DWI), which is responsible for regulating drinking water quality.**



1. Understanding the chemistry of fluoride in water

Naturally present in all water supplies at low concentrations

Fluoride occurs naturally in all water supplies. Artificial water fluoridation is the process of adjusting the naturally occurring fluoride in water supplies to a level that is known to benefit teeth: one part of fluoride per one million parts of water (1 ppm). Another way of expressing this value is 1 milligram of fluoride per litre of water (1mg/l). This is a level that occurs naturally in many places throughout the world. In the UK, for example, the water supply for Hartlepool has a natural fluoride content a little higher than this at around 1.2 ppm. In some parts of Essex, it may sometimes be higher still.

Abundant in the earth's crust

Fluorides are abundant in the earth's crust and are present in the environment largely as a result of volcanic and industrial activity. Fluoride is present in water supplies as a result of having been dissolved out of the rocks and soils over which the water has travelled.

Inorganic and organic fluorides

There are two normal forms of fluoride, *inorganic* and *organic*; however, in dentistry, medicine and public health, only the inorganic form (which yields the fluoride ion) is important. Inorganic fluoride also occurs in two different forms: *ionic fluoride*, and *nonionic fluoride*. Importantly, it is the concentration of *ionic fluoride* in solution that is referred to (generally in parts per million - ppm) when we talk of the fluoride concentration of a water supply. The concentration of fluoride in water is analysed by the *fluoride ion specific electrode* which measures free fluoride ions, not fluoride bound to metal ions such as calcium, magnesium, iron or aluminium (1).

*In developed countries with
temperate climates, there is
no evidence of harm to human
health from water-borne fluoride.*

Factors affecting the natural fluoride concentration in ground waters

The natural fluoride concentration of ground waters is affected by the availability and solubility of fluoride-containing minerals and the porosity of rocks and soils over which the water passes. It is also affected by temperature, pH, and the presence of other minerals such as calcium, aluminium and iron which may combine with the fluoride ion.

Ground waters in the United States have been reported to have fluoride concentrations of up to 67 parts per million, and in parts of India and Africa much higher concentrations have been reported. Most surface waters contain much lower fluoride concentrations - usually less than 0.1 ppm, but reaching 1.0 ppm in some rivers in the UK, Spain, Canada, Japan and Finland (1).

In parts of some undeveloped countries where the climate is hot, and safe water supplies are unavailable, very high natural levels of fluoride in drinking water can cause damage to the bones and teeth of humans and animals if consumed over many years. (Such water supplies are often also contaminated with unsafe levels of other natural chemicals including arsenic, iron and salts.)

However, in developed countries with temperate climates such as the UK, United States and Canada, there is no evidence of harm to human health from water-borne fluoride - even in populations where the level of fluoride in drinking water is in excess of that known to be optimal for dental health - 1 part of fluoride per million parts of water (1 ppm) (2) (3).

The laws of chemistry dictate that fluoride ions in water are identical whether they occur naturally in the water or are added,

2. Expert review of the chemistry and uptake of fluoride in drinking water

The laws of chemistry dictate that fluoride ions in solution in water are identical whether they occur naturally in the water or are added. Since artificial water fluoridation began in the United States in 1945, scientists have therefore believed that the body's uptake of fluoride from water is the same whether the 1 part per million fluoride level is naturally occurring or artificially adjusted.

On the other hand, opponents of water fluoridation claim that the body's uptake of fluoride from naturally fluoridated water is different from that of artificially fluoridated water, and that artificially fluoridated water is in some way harmful.

Because of such claims, and to improve our understanding of the chemistry of water fluoridation, in 2002 experts at Water Research Centre (WRc-NSF) were asked by the British Fluoridation Society to provide an independent expert review of the chemistry and uptake (bioavailability) of fluoride in drinking water.

The full report of the WRc-NSF study (4) is available on the British Fluoridation Society website (<http://www.bfsweb.org/documents/wrcreport.pdf>). Below is a lay summary of the report that has been reviewed and approved by the authors of the original study.

3. WRc-NSF study aims

The aim of the WRc-NSF study was to answer the following key questions:

1. Are there differences in uptake of fluoride naturally present and that added to the water supply?
2. Does water hardness affect the uptake of fluoride in humans?
3. Does fluoride at around 1 part per million (1 ppm) affect the uptake of other constituents of water, e.g., aluminium?
4. Does fluoride at around 1 ppm affect the possibility of interactions either between the constituents of water, or between water and the pipes through which it travels?
5. Do other components of the artificially added fluoride compounds increase the toxicity of water?

Study method

Questions 1 to 4 were addressed by calculating the outcome of chemical reactions between fluoride and other water constituents and interpreting the results in terms of bioavailability (uptake). The outcome of chemical reactions (the 'speciation' of the resulting mixture of chemicals dissolved in water) was calculated using the accepted scientific method of *chemical equilibrium and mass balance modelling*. Based upon the results, the potential effects on bioavailability (uptake) were then assessed.

In drinking water there are many chemical reactions taking place at any one time, and although it is possible to model all of these reactions simultaneously, the models become complicated and can give results that are difficult to interpret. The WRc-NSF scientists thought that the results for each individual substance would be more clear-cut. Therefore, to keep the chemical models simple and to make the results easier to understand, separate models were constructed to address each question.

Question 5 was addressed by investigating the impurities that would be added. Calculations were based on product specifications and actual product quality data for fluoridation chemicals.

All waters contain fluoride at some concentration as a result of having been dissolved out of the rocks over which the water has travelled.

4. WRc-NSF study results

Added fluoride was shown to be identical to 'natural' fluoride

Natural fluoridation

All waters contain fluoride at some concentration as a result of having been dissolved out of the rocks over which the water has travelled. These include fluor spar (natural calcium fluoride - CaF_2). When minerals such as fluor spar dissolve in water the molecules split up to produce calcium and fluoride ions - shown in the equation below as 2F^- .



Artificial fluoridation

In the UK only two fluoride compounds are permitted for the adjustment of fluoride levels in water to improve dental health (water fluoridation). They are hexafluorosilicic acid (H_2SiF_6), which is a liquid, and disodium hexafluorosilicate (Na_2SiF_6), which is a crystalline powder.

In practice, the powder - disodium hexafluorosilicate - is used far less commonly than the liquid, hexafluorosilicic acid. When hexafluorosilicic acid is added to water, it splits up and thereby releases fluoride ions (shown in the equation below as 6F^-). The overall reaction is:



With disodium hexafluorosilicate, the reaction is:



The fluoride ion produced from artificial fluoridation behaves identically to the fluoride ion present naturally in water. Chemically, there is absolutely no difference between artificial and natural fluoridation.

Is the fluoride the same in natural and artificially fluoridated water?

To check whether the fluoride added to water is the same as that which is naturally present, it was necessary to establish the extent to which the hexafluorosilicate ion (SiF_6^{2-}) splits up to form fluoride ion (F^-) and silicic acid ($\text{Si}(\text{OH})_4$) – a process known as the *dissociation reaction*. The calculation covered the range of pH levels normally encountered in water supplies (a pH below 7 indicates acidity, a pH in excess of 7 indicates alkalinity), and the 'worst case' in terms of the relevant chemical reactions (by using the smallest value hydrolysis constant). The results showed that, effectively, all of the hexafluorosilicate would dissolve to form free fluoride ion (F^-).

Next, the rate at which the *dissociation reaction* takes place was calculated to check whether the process of splitting will take place within the timescale relevant to water treatment and distribution (hours to days). The conclusion was that the process is complete by the time the water reaches the consumer's tap. In other words, the fluoride ion produced from artificial fluoridation will behave identically to the fluoride ion naturally present in water supplies. It means that, chemically, there is absolutely no difference between artificial and natural fluoridation.

The effects of calcium and magnesium (water hardness) and sodium on fluoride availability were calculated

The hardness of water is determined by the amount of dissolved calcium and magnesium. A typical ratio of 1:5 magnesium to calcium was used to calculate the proportion of free fluoride ion in relation to the concentration of calcium and magnesium.

Water hardness may be expressed in a variety of units. In the UK it is commonly expressed in terms of milligrams per litre (mg/l) as calcium, or mg/l as calcium carbonate (CaCO_3). The hardness in mg/l calcium carbonate is 2.5 times the hardness in mg/l as calcium.

Water hardness is often classified by descriptive words, as shown in Table 1.

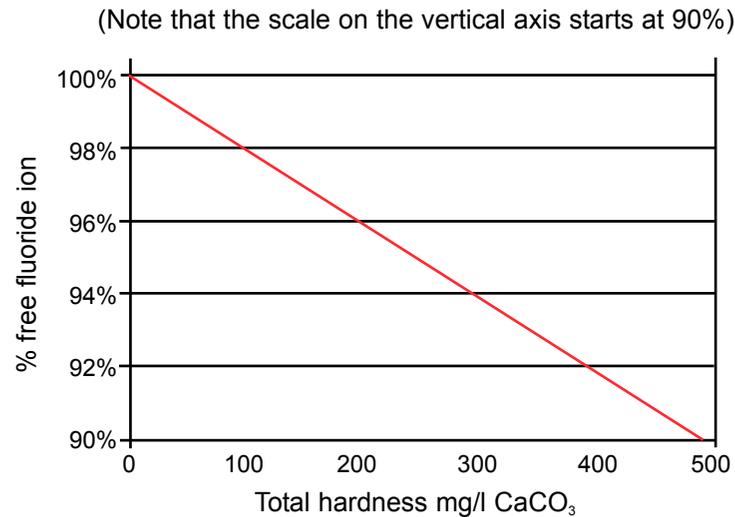
Description of water	Hardness in mg/l as calcium carbonate	Hardness in mg/l as calcium
Soft	Up to 50	Up to 20
Moderately soft	50-100	20-40
Slightly hard	100-50	40-60
Moderately hard	150-200	60-80
Hard	200-300	80-120
Very hard	Over 300	Over 20

The hardness of water supplies in the UK covers a wide range. Some examples are given in Table 2 below. It should be noted, however, that these figures are approximate, and that even within quite small geographical areas there can be large differences in water hardness. Hardness can also vary seasonally.

Location	Total hardness in mg/l as calcium carbonate <u>approximate</u>
Glasgow	20
Birmingham	50
Newcastle	120
London	300
Hartlepool	450

In the WRc-NSF study, calculations were made for water hardness in the range 0 to 500 mg/l calcium carbonate, which more than covers the range that occurs in the UK. The results of the calculations are shown in Figure 1.

Figure 1: Effect of water hardness on fluoride ion concentration



- 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 present that would be bound to fluoride would be very small indeed – for example, in water with 1 ppm fluoride, less than 0.05% of the calcium would be present as calcium fluoride.
- It was therefore concluded that the effect of water hardness on the uptake of fluoride would be very small.
- Using a similar approach, it was 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 fluoride ion.

Possible interactions with aluminium, iron, copper and lead were calculated

The interactions between fluoride and the dissolved trace metals of aluminium, iron, copper and lead were examined in a similar way to that described for calcium and magnesium above.

Aluminium

Aluminium is naturally present in some waters but occurs in drinking water predominantly through the use of aluminium sulphate in the process of water treatment to remove cloudiness. The added aluminium forms aluminium hydroxide, removing suspended material and some dissolved substances. The precipitated aluminium hydroxide is removed by settlement and filtration. The residual aluminium concentration passing into the water supply should not exceed 0.05 mg/l (the maximum permitted is 0.2mg/l). However, aluminium hydroxide can accumulate as a deposit within distribution systems (e.g., in dead ends).

Calculations were made using a total available fluoride concentration of 1 ppm. The results showed that fluoride forms strong complexes with aluminium. The fluoride complexes accounted for a substantial proportion of the dissolved aluminium only at pH values less than 7.

This indicates that, in the presence of slightly acidic water, fluoride could dissolve aluminium deposits within the distribution system. However, since virtually all UK water supplies are likely to have pH values of greater than 7, this is unlikely to be a problem in practice.

Iron

Iron is present naturally in many water sources. It is removed during water treatment. Iron in water supplies may also be derived from corrosion of iron mains, but any concentrations present in water do not present any risk to health. Iron compounds are used in water treatment to remove cloudiness. As far as aluminium is concerned, the residual iron concentration passing into the water supply should not exceed 0.05 mg/l (the maximum permitted is 0.2mg/l). However, concentrations above this level do occur and iron hydroxide can accumulate as a deposit within distribution systems (e.g., in dead ends).

Calculations were made using a total available fluoride concentration of 1 ppm. The results showed that less than 0.005% of the iron is present as fluoride complexes. It means that the presence of fluoride at 1 ppm has essentially no effect on the solubility of iron. Fluoride will not, therefore, affect the bioavailability of iron.

Copper

Traces of copper, which are not significant to health, occur naturally in many water sources. Higher concentrations may occur at consumers' taps as a consequence of copper pipes. The concentrations present in water do not present any risk to health. The maximum level permitted is 3 mg/l, though in practice the levels in water supplies are very much less than this.

Under all the conditions examined by the WRc-NSF scientists, the reaction with fluoride accounted for less than 0.1% of the dissolved copper. It was found that, even under conditions of low pH and low alkalinity (pH 6, alkalinity 10 mg/l as CaCO₃), the presence of 1 ppm fluoride would only increase copper solubility by 0.05%. Fluoride will not, therefore, affect the bioavailability of copper.

Lead

Lead is not normally present in water sources but may be present at consumers' taps if the water flows through lead pipes. Calculations were made using a total available fluoride concentration of 1 ppm, and at a range of pH values and alkalinity. Under all the conditions, the reactions with fluoride accounted for less than 0.5% of the dissolved lead. Even under conditions of low pH and low alkalinity, it was found that the presence of 1 mg/l fluoride would only increase lead solubility by 0.5%. Fluoride will not, therefore, affect the bioavailability of lead.

A different, more detailed study, by scientists in the United States examined in great depth the possibility of lead concentrations in drinking water being increased following fluoridation using hexafluorosilicate. A sophisticated model that considered all possible reactions together was used (5). They considered the possible reactions of lead with fluoride, and found that the lead fluoride complexes accounted for less than 1% of the total dissolved lead – i.e., essentially the same result as reported by the WRc-NSF scientists.

No credible evidence exists to show that water fluoridation has any quantifiable effects on the solubility, bioavailability or reactivity of lead or lead compounds.

The US scientists found that the concentration of lead fluorosilicate (PbSiF_6) would be vanishingly small - one molecule in 1,000 litres of water at pH 6. They also showed that the small pH drop caused by fluoridating water with hexafluorosilicic acid has an insignificant effect on dissolving lead.

Overall, they concluded that: "No credible evidence exists to show that water fluoridation has any quantifiable effects on the solubility, bioavailability, bioaccumulation or reactivity of lead(0) or lead(II) compounds."

Interactions with other chemical reactions and the distribution system were considered

It has been shown above that, with the exception of aluminium, the major and minor chemicals present in water do not react to any significant extent with fluoride. This means that, at the concentrations relevant to fluoridation, the fluoride ion could not cause significant interactions between other compounds (e.g., by forming chemical bridges).

The WRc-NSF scientists found very little published information on the effects of fluoridation on distribution system corrosion. They thought this was probably because any such effects are negligible and do not cause any problems in practice. They found that, while the use of hexafluorosilicic acid for water fluoridation will cause a reduction in both pH and alkalinity, the low dose used in practice means that such effects are likely to be negligible, except in very soft, poorly buffered, waters.

Poorly buffered water is water with little capacity to resist a change of pH if acid or alkali is added. In fresh waters, the alkalinity (carbonate and bicarbonate) provides the buffer capacity. Hard waters almost invariably have high alkalinity and consequently greater buffer capacity.

Calculations show that fluoridation to a concentration of 1ppm using hexafluorosilicic acid 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 6.96. Fluoridation using sodium hexafluorosilicate will only slightly reduce pH and alkalinity.

The WRc-NSF scientists noted that Urbansky and Schock (5), who modelled the effects on pH and buffer capacity, support this conclusion. In practice, however, water suppliers add alkali to adjust the pH to an appropriate value before the water leaves the water treatment works. Virtually all UK public water supplies therefore have pH greater than 7.

The WRc-NSF scientists concluded that it seems unlikely that fluoridation would have a noticeable effect on corrosion.

The quantities of trace metals added with fluoridation chemicals were calculated both for the minimum specification (worst case) and actual quality of fluoridation chemicals

The impact fluoridation has on concentrations of trace metals in drinking water was determined by considering the specifications for fluoridation chemicals (the 'worst case'), and by calculations based upon actual product quality.

European standards for water treatment chemicals under European Union legislation (ENs) are published by the British Standards Institution as BS ENs.

Water treatment chemicals which conform to 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 (6).

European standards for hexafluorosilicic acid and sodium hexafluorosilicate have been adopted and published by the British Parameter Units Value (mg/kg is the same as parts per million). See tables 3 and 4 on the following page.

Table 3 European standard BS EN 12175 for hexafluorosilicic acid
(mg/kg is the same as parts per million)

Parameter	Units	Value
H ₂ SiF ₆	% m/m	spec. ±5
Free acid (HF)	mg/kg product max.	1.5
Phosphate (P ₂ O ₅)	mg/kg product max.	0.75
As (arsenic)	mg/kg H ₂ SiF ₆ max.	400
Cd (cadmium)	mg/kg H ₂ SiF ₆ max.	40
Cr (chromium)	mg/kg H ₂ SiF ₆ max.	400
Hg (mercury)	mg/kg H ₂ SiF ₆ max.	10
Ni (nickel)	mg/kg H ₂ SiF ₆ max.	400
Pb (lead)	mg/kg H ₂ SiF ₆ max.	400
Sb (antimony)	mg/kg H ₂ SiF ₆ max.	80
Se (selenium)	mg/kg H ₂ SiF ₆ max.	80

Table 4 European standard BS EN 12174 for disodium hexafluorosilicate
(mg/kg is the same as parts per million)

Parameter	Units	Value
Na ₂ SiF ₆	% m/m min.	98
Moisture	% m/m product max.	0.3
Insolubles	% m/m product max.	0.5
As (arsenic)	mg/kg product max.	400
Cd (cadmium)	mg/kg product max.	40
Cr (chromium)	mg/kg product max.	400
Hg (mercury)	mg/kg product max.	10
Ni (nickel)	mg/kg product max.	400
Pb (lead)	mg/kg product max.	400
Sb (antimony)	mg/kg product max.	80
Se (selenium)	mg/kg product max.	80

Standards Institution: BS ENs 12174 (7), and 12175 (8)

These standards are listed in the latest List of Approved Products (9). The standards lay down requirements for product purity that are summarised in Tables 3 and 4 above.

Using hexafluorosilicic acid as an example, it can be seen from Table 3 that to meet European and British Standards, the product must contain no more than 400 mg per kg (400 parts per million) of arsenic, 40 mg per kg of cadmium, 10 mg per kg of mercury, 400 mg per kg of lead and so on.

On the face of it the presence of such toxic substances in a product to be added to drinking water supplies may be alarming to the lay reader. However, it is important to be aware that:

- To achieve the optimal concentration of one part of fluoride per million parts of water, the product is diluted approximately 170,000 times.

- Because of the high dilution factor, the levels of any impurities added as a result of fluoridation are very small indeed, and have no discernible impact on the toxicity of drinking water. For example, fluoridation using hexafluorosilicic acid will generally *add less than 1% of the maximum permitted levels of trace metals to water supplies* (see below).
- Like fluoride, some of these substances (e.g., arsenic) are naturally present in many water supplies. However, stringent European and British drinking water quality regulations - which are rigorously enforced - ensure that maximum permitted levels are far too low to be harmful (see below).

Table 5 Impurities added by dosing hexafluorosilicic acid

(mg/kg is the same as parts per million, and micrograms per litre or µg/l is the same as parts per billion)

Element	Maximum permitted level in product, mg/kg H ₂ SiF ₆	µg/l (micrograms per litre) added at 1 mg/l fluoride dose	Parametric Value	% of permitted level added
			(permitted level) in micrograms per litre (µg/l)	
As (arsenic)	400	0.51	10	5.1
Cd (cadmium)	40	0.05	5	1.0
Cr (chromium)	400	0.51	50	1.0
Hg (mercury)	10	0.01	1	1.0
Ni (nickel)	400	0.51	20	2.5
Pb (lead)	400	0.51	10	5.1
Sb (antimony)	80	0.10	5	2.0
Se (selenium)	80	0.10	10	1.0

Table 6 Impurities added by dosing disodium hexafluorosilicate

(mg/kg is the same as parts per million, and micrograms per litre or µg/l is the same as parts per billion)

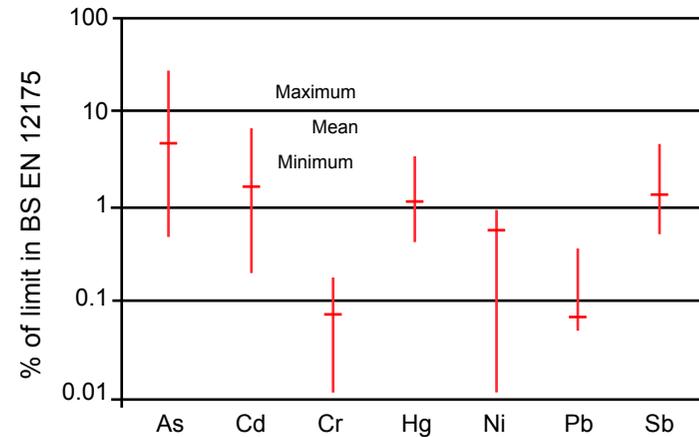
Element	Maximum permitted level in product, mg/kg H ₂ SiF ₆	µg/l (micrograms per litre) added at 1 mg/l fluoride dose	Parametric Value	% of permitted level added
			(permitted level) in micrograms per litre (µg/l)	
As (arsenic)	400	0.67	10	6.7
Cd (cadmium)	40	0.07	5	1.3
Cr (chromium)	400	0.67	50	1.3
Hg (mercury)	10	0.02	1	1.7
Ni (nickel)	400	0.67	20	3.3
Pb (lead)	400	0.67	10	6.7
Sb (antimony)	80	0.13	5	2.7
Se (selenium)	80	0.13	10	1.3

The maximum concentration of a contaminant that could be added to drinking water as a result of adding a fluoride dose of 1 ppm was calculated. These are shown in tables 5 and 6, with the European permitted levels (parametric values) for comparison.

Using arsenic and lead as examples, it can be seen that at a dose of 1 mg/l as F (the highest that would be used in practice), only about 5% of the permitted level for these parameters could be added by a product that contained the maximum permitted levels of trace metals (see shaded areas in table 5).

In practice, trace metal contents are lower than the limits in the BS EN standards permit. Figure 2 shows a summary of data on hexafluorosilicic acid supplied by Hydro Chemicals, based on monthly analyses over the period January 1996 to June 2000. The vast majority of fluoridation plants in the UK use hexafluorosilicic acid.

Figure 2: Summary of quality of hexafluorosilicic acid



The maximum trace metal concentrations found were approximately 20% of the limit in the BS EN standard (data for selenium were not available). Therefore, because of dilution, using hexafluorosilicic acid for fluoridation will generally 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 Organisation as being safe for a lifetime's exposure (consumption of 2 litres of water per day over 70 years).

5. Conclusions of the WRc-NSF study

- In terms of chemistry and bioavailability (uptake), there is no difference between added and 'natural' fluoride.
- The effect of calcium and magnesium (water hardness) and sodium - on the chemical reactions and hence uptake of fluoride - is very small.
- Fluoride forms strong bonds with aluminium, so effects on uptake are theoretically possible in the presence of slightly acidic water. However, since virtually all UK water supplies are likely to have pH values of greater than 7, this is unlikely to be a problem in practice.
- The presence of fluoride at a concentration of 1 ppm will have practically no effect on the chemical reactions and uptake of iron, copper or lead.
- There is no plausible mechanism by which fluoride could interact with other chemical reactions in drinking water. Fluoridation will therefore have a negligible impact on the corrosiveness of water in the distribution system.
- The traces of impurities added as a result of fluoridation are very small and would have no measurable impact on the toxicity of drinking water.

6. The manufacture and regulation of the chemicals used for water fluoridation

Permitted chemicals

Drinking water safety is taken very seriously in the UK. Very strict European and UK regulations govern what can be added to public water supplies.

As has already been described, European standards for water treatment chemicals under EU legislation (ENs) are published by the British Standards Institution as BS ENs. Only water treatment chemicals which conform to 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 (6).

The Drinking Water Inspectorate (DWI), which is part of the Department for Environment, Food and Rural Affairs (DEFRA), is responsible for enforcing the standards, and does so by undertaking regular checks.

Only two compounds of fluoride are permitted for artificial fluoridation in the UK (10. 11):

- Hexafluorosilicic acid (H_2SiF_6), also known as fluorosilicic acid
- Disodium hexafluorosilicate (Na_2SiF_6), also known as sodium fluorosilicate

These compounds achieve the desired concentration of fluoride (1 part per million) reliably and safely, and must meet Department of Environment purity specifications (6).

How the chemicals are produced

The chemicals used for water fluoridation are specifically manufactured to exacting quality standards. The manufacturing process involves recovery of the product from a vapour phase, which ensures a high degree of purity. The end result is a valuable and useful resource that meets very high quality specifications.

The manufacturing process

The vast majority of fluoridation plants in the UK use hexafluorosilicic acid, which is a liquid, as the fluoridating agent.

The raw materials

Fluoride is found in a solid form in minerals such as fluorspar, cryolite and apatite (pictured from left to right).

Fluorspar (also called fluorite) is found in most parts of the world. It is a mineral containing between 30 to 98 percent calcium fluoride.

Cryolite is a compound of aluminium, sodium, and fluoride. Because of its low melting point, it is preferred for industrial use, but is not a major source of fluoride for water fluoridation.

Apatite is a deposit of a mixture of calcium compounds, including calcium phosphates, calcium fluorides, and calcium carbonates. Apatite contains between 3 to 7 percent fluoride and is the main source of fluorides used in water fluoridation.



To obtain *hexafluorosilicic acid* (H_2SiF_6):

- The fluoride-containing rock is ground up and treated with sulphuric acid, producing hydrofluoric acid gas (HF).
- The HF gas then begins a purification process that involved washing, cooling, condensation, and, finally, distillation (rectification).
- The HF is then reacted with silica to produce hexafluorosilicic acid with a concentration of 37 to 42 per cent.

By neutralising hexafluorosilicic acid with sodium carbonate and precipitating the solid matter, manufacturers can readily convert liquid hexafluorosilicic acid into the powder *disodium hexafluorosilicate* (Na_2SiF_6).

As has previously been discussed in detail, trace elements such as lead and arsenic are present in minute quantities in fluoride compounds. This is because fluoride compounds are derived from naturally occurring minerals, and such trace elements are always present in minerals of this type.

However, maximum levels of these trace elements - including arsenic and lead - are laid down as standards. Details are incorporated in the product specifications in the Code of Practice (6).

It is likely that few people realise that arsenic occurs naturally in some drinking waters – or that in the UK some natural levels are above the permitted level of 10 parts per billion and therefore must be reduced to comply with Water Quality Regulations (12).

Fortunately, the levels of such unwanted trace elements in the fluoride compounds used for fluoridation are minute, and become immeasurable when diluted thousands of times to achieve 1 part per million of fluoride in water. Fluoridation therefore makes no measurable contribution to the concentration of these substances in water supplies.

Common misconceptions

It is often claimed by opponents of fluoridation that the aluminium and phosphate fertiliser industries have a vested interest in promoting water fluoridation. It is perhaps worthwhile addressing those claims here.

The phosphate fertiliser industry

Apatite is the raw material used in the manufacture of phosphate fertilisers. Fluorine for the manufacture of fluorides for water fluoridation is recovered from this process. The manufacturing process to produce fluorosilicic acid for water fluoridation involves recovery of the product from a vapour phase, which ensures a high degree of purity. The product is therefore manufactured *in tandem* with the production of phosphoric acid, and can be described as a 'co-product'. It would, however, be equally valid to describe phosphate fertilisers as co-products of the manufacture of fluorosilicic acid, since both are valuable products.

Prior to 1987, when hexafluorosilicic acid was produced in the UK for water fluoridation, manufacture was intermittent to match market need and represented only about 10% of the total fluorine that could be extracted from the process.

Since production in the UK ceased, chemicals companies have imported supplies of hexafluorosilicic acid to service the established market. The product is Quality Assured to BS5750, and as already stated, the specification conforms to that given in the Department of the Environment's Code of Practice on Technical Aspects of Fluoridation of Water Supplies.

The aluminium industry

The basis of the claims that the aluminium industry promotes fluoridation in order to dispose of its toxic waste seems to be based on a tenuous link more than 40 years ago in the United States. In the 1940s, The Aluminium Company of America (ALCOA) acquired a chemical manufacturing plant which produced fluoride compounds by the method described above (not as a waste product of aluminium production). ALCOA was then using sodium fluoride as a catalyst in the aluminium smelting process, but soon replaced sodium fluoride with less costly fluoride

Fluoride compounds used for water fluoridation are not now, and have never been, obtained as industrial waste. They are manufactured to exacting quality standards and must meet Department of the Environment purity standards.

compounds. ALCOA sold the chemical plant in the early 1950s. Its last sales of sodium fluoride were in 1952. Nowadays, the aluminium industry is the largest *user* of fluoride compounds, and has no interest in promoting water fluoridation whatsoever.

Summary

Only two compounds of fluoride are permitted for artificial fluoridation in the UK: hexafluorosilicic acid (H_2SiF_6) and disodium fluorosilicate (Na_2SiF_6). These compounds are manufactured to exacting quality standards and must meet Department of the Environment purity specifications. Fluoride compounds used for water fluoridation are not now, and have never been, obtained as industrial waste.

7. Safety at the water treatment works

A Drinking Water Inspectorate Code of Practice ensures that safety is the prime consideration when fluoride is added to water (6).

Water companies in the UK have over 50 years' experience of water fluoridation schemes. Around the world, there are thousands of highly successful fluoridation schemes in operation. For example, in the United States alone - the country with the largest number of people drinking water with added fluoride - there are over 16,000 individual water systems operating fluoridation schemes.

A wealth of practical experience

Water suppliers have accumulated a wealth of practical experience in managing the fluoridation process safely and efficiently. In the UK, the first schemes were introduced on an experimental basis in Anglesey, Watford, Kilmarnock and Andover in the mid-1950s. The first large-scale scheme started in Birmingham and Solihull in 1964. Another followed a few years later in Newcastle.

In all operations concerning the process of fluoridation at the water treatment plant, the emphasis is very much on safety. The aim throughout is to make absolutely certain that only the right amount of fluoride is added to the water.

UK water companies that operate fluoridation schemes

UK water companies that are currently operating fluoridation schemes include Anglian Water; Northumbrian Water; Severn Trent Water; South Staffordshire Water; and United Utilities.

UK water suppliers that have in the past operated fluoridation schemes include: Department of the Environment for Northern Ireland; Thames Water; Welsh Water; and Yorkshire Water.

Code of practice

Strict operational criteria are laid down in the 2005 '*Code of Practice on Technical Aspects of Fluoridation of Water Supplies*' issued by the Drinking Water Inspectorate on behalf of the Department of the Environment (6). These are designed to ensure that:

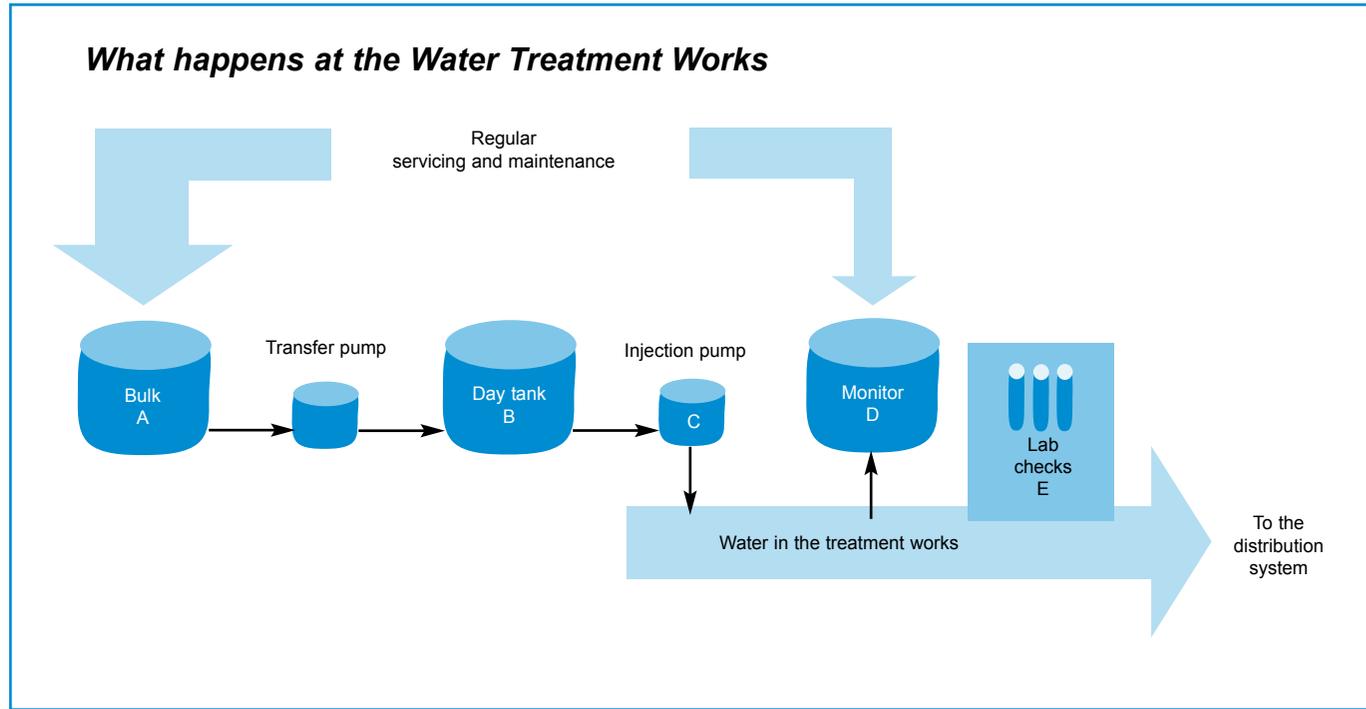
- Safety is paramount in the delivery and storage of fluoride chemicals and at all stages in the water fluoridation process.
- The fluoride content of the water leaving the treatment works does not exceed 1.5 parts per million at any time (in accordance with the Water Supply (Water Quality) Regulations 2000, which apply to both naturally fluoridated and artificially fluoridated water).

How fluoride is added to the water supply

During the process of water treatment at the water treatment works, a solution of fluoride is injected into water under close control. Although the physical layout of the fluoridation equipment will vary between treatment works, the essential principles of the design and operation are determined by the need to meet the operational and Health and Safety criteria laid down in the Code of Practice. These will be common to all fluoridation plants and include:

- (a) bulk storage tanks suitably constructed, located, and labelled, to receive deliveries and store the fluoride liquid;
- (b) working storage (day tank), which holds only enough fluoride for one day's operation;
- (c) an injection pump to deliver fluoride into the water at the rate required at a point beyond which good mixing will be achieved before the water leaves the water treatment works;
- (d) a continuous recording fluoride monitor, linked to an appropriate alarm system, and automatic plant shut down to prevent over-dosing;
- (e) a programme of regular supervision, sampling and reporting;
- (f) regular servicing and maintenance.

8. What happens at the water treatment works



One day's supply at a time

The fluoride is delivered by tanker and kept in a bulk storage tank (A in the diagram). Every day, the right amount needed for one day's operation is transferred to a separate, smaller 'day tank' (B in the diagram above and also pictured left). Both tanks are specially constructed from acid resistant material, and the day tank can hold a maximum of only one day's supply at a time.





Pump operating at a maximum capacity

A second safety feature is the injection pump that transfers the fluoride liquid from the day tank into the mains (C in the diagram). The pump is automatic and its pumping rate is proportional to the flow of water. Even when operating at maximum capacity, it is only capable of adding fluoride at the rate required in relation to the flow of water through the mains. If the water flow reduces or stops, the pump will also stop. Furthermore, should the pump break down or malfunction, the result would be the addition of less than the required amount of fluoride, not more.

Monitoring 24 hours a day

The third safety feature is the continuous recording fluoride monitor (D in the diagram and also pictured left) - every second of every day the fluoride level in the water is monitored at a sampling point which is some distance from the injection pump, but before water leaves the treatment works and enters the distribution system. The process is automatic and is carried out by equipment which itself is regularly checked to ensure its accuracy. Nowadays, standard practice is for there to be two monitors. This enables data to be cross-checked. It also safeguards the continuity of monitoring in the event of a malfunction in one of the two monitors.

If at any time the fluoride level should exceed the permitted level, an electronic warning is transmitted to the control room and the whole plant is automatically shut down. The monitor also incorporates a fail-safe mechanism that shuts down the fluoridation plant if the monitor itself or 'controller' becomes faulty.

Laboratory checks

Finally, there is a double check in the laboratory, with samples taken regularly from several taps in the local distribution system for testing and analysis (E in the diagram). Reports are sent to the directors of public health of the districts covered by the fluoridation scheme. This is in addition to the general sampling and monitoring required under water quality regulations (12).

The record on safety

Many of the chemicals used to treat our water supplies are highly toxic in their concentrated forms, so the possibility always exists for accidents resulting in harm to people working with those chemicals.

Of course, the water industry takes its health and safety responsibilities very seriously and, fortunately, serious accidents involving water treatment chemicals are rare. Since fluoridation began in the UK in the in the mid-1950s, there have been no such accidents involving fluoride.

Worldwide there are many thousands of fluoridation schemes in operation – the earliest dating from 1945. Water suppliers have therefore accumulated a wealth of practical experience in managing the fluoridation process safely and efficiently.

The practice of adjusting the natural level of fluoride in drinking water to improve dental health began in 1945 in the city of Grand Rapids in the US State of Michigan. Since then, hundreds of millions of people worldwide have regularly consumed fluoridated water – including an estimated 370 million today.

Overall, water fluoridation has an excellent safety record. However, some serious spillage and overfeed incidents have been reported in the United States, though these are extremely rare (13).

In the United States, many fluoridation plants serve very small communities such as schools and relatively undeveloped remote villages. Training and supervision of water plant operators in such locations tends to be less stringent than in the highly regulated UK water industry and equipment such as continuous recording fluoride monitors is not the norm.

Incidents are always investigated, and often found to have resulted from lack of operator training and supervision, and bad or poor equipment design. In order to minimise the risk of such accidents, for many years the US Public Health Service Division of Oral Health at the Centers for Disease Control and Prevention (CDC) has played a major role in providing educational material and training courses for States and water companies to help them develop and maintain standards of competence among their water plant operators.

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