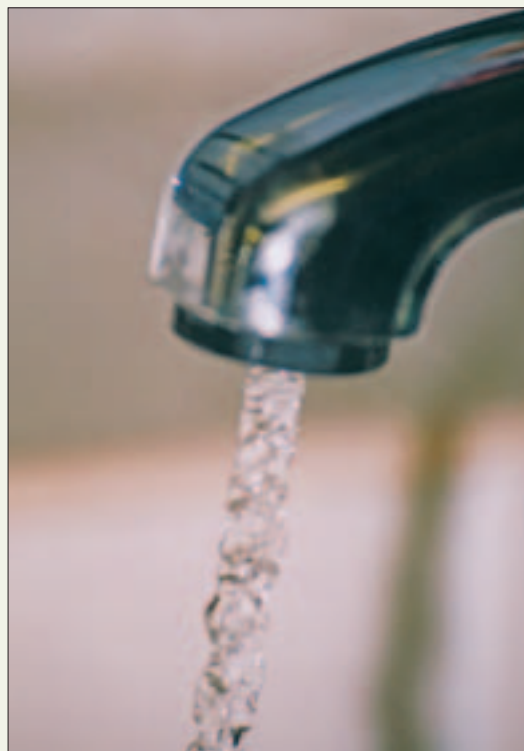


Key points

- 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 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 USA. Since then hundreds of millions of people worldwide have regularly consumed artificially fluoridated water – including nowadays around 350million, over 160 million of them in the USA.
- The fluoride ion produced from artificial fluoridation behaves identically to the fluoride ion naturally present in water supplies, which means that, chemically, there is no difference between artificial and natural fluoridation.
- Water fluoridation has an excellent safety record.



Understanding the chemistry of fluoride in water

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: 1 part of fluoride to one million parts of water (1 ppm)ⁱ. 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, and in some parts of Essex it was higher still.

Fluorides are abundant in the earth's crust and are present in the environment largely due to 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. 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 however, 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].

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, in addition to 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].

ⁱ Parts per million (ppm) is the same as milligrams per litre (mg/l or mg l⁻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, USA and Canada, there is no evidence of harm to human health from waterborne 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 for every one million parts of water (1 ppm) [2]. Many studies of the health of populations in temperate climates drinking water with natural fluoride concentrations up to 8 ppm have found no evidence of harmful effects [3].

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; therefore scientists have believed since artificial water fluoridation first began in the United States in 1945, that the body's uptake of fluoride from water is the same whether the fluoride level is naturally elevated or artificially adjusted. However, opponents of water fluoridation increasingly 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 WRC-NSF were asked 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 (www.bfsweb.org/wrcreport.pdf). Below is a lay summary of the report that has been reviewed and approved by the authors of the original study.

Study aims

The aim of the 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) were calculated using the accepted scientific method of '*chemical equilibrium and mass balance modelling*'. The potential effects on bioavailability (uptake) were then assessed based upon the results.

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 based on product specifications and actual product quality data for fluoridation chemicals.

Results

1. 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 such as 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 to improve dental health (water fluoridation). They are hexafluorosilicic acid (H_2SiF_6) which is a liquid, and sodium hexafluorosilicate (Na_2SiF_6) which is a crystalline powder. However, in practice the powder, sodium hexafluorosilicate, is used far less commonly than the liquid, hexafluorosilicic acid.

When hexafluorosilicic acid is added to water it splits up releasing fluoride ions (shown in the equation below as 6F^-), the overall reaction being:



With sodium hexafluorosilicate the reaction is:



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 (Si(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 consumers tap.

In other words the fluoride ion produced from artificial fluoridation will behave identically to the fluoride ion naturally present in water supplies, which means that, chemically, there is absolutely no difference between artificial and natural fluoridation.

2. 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.

Table 1 Classification of water hardness

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 – 150	40 – 60
Moderately hard	150 – 200	60 – 80
Hard	200 – 300	80 – 120
Very hard	over 300	Over 120

The hardness of water supplies in the UK covers a wide range, and 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; also, hardness can vary seasonally.

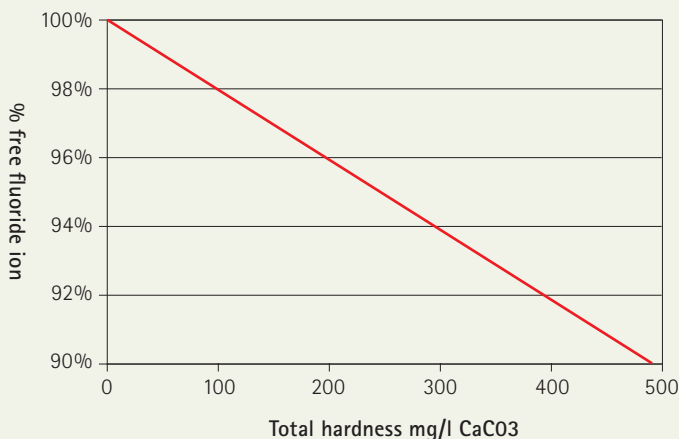
Table 2 The hardness of some UK water supplies

Location	Total hardness in mg/l as calcium carbonate approximate
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

(Note that the scale on the vertical axis starts at 90%)



- 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.

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

The interactions between fluoride and the dissolved trace metals 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 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 for aluminium, the residual iron concentration passing into 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; which means that the presence of fluoride at 1 ppm has essentially no effect on the solubility of iron. Therefore fluoride will not affect the bioavailability of iron.

Copper

Traces of copper, which are not significant to health, occur naturally in many water sources and 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 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%. Therefore fluoride will not affect the bioavailability of copper.

Lead

Lead is not normally present in water sources but may be present at consumers' taps if lead pipes are present.

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 examined 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%. Therefore fluoride will not 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. The US scientists found that the concentration of lead fluorosilicate (PbSiF₆) would be vanishingly small – one molecule in 1000 litres of water at pH 6. They also showed that the small pH drop caused by fluoridating 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.'

4. Interactions with other chemical reactions and the distribution system were considered.

It has been shown in Sections 2 and 3 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. This they thought was probably because any such effects are negligible and do not cause any problems in practice. They found that while fluoridation using hexafluorosilicic acid 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 bufferedⁱ, waters. Calculations show, for example, that fluoridation to 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 CaCO₃). In harder water (alkalinity 200 mg/l as CaCO₃) 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; therefore virtually all UK public water supplies have pH greater than 7. The WRc scientists concluded that it seems unlikely that fluoridation would have a noticeable effect on corrosion.

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

ⁱ 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.

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 hexafluorosilicic acid have recently been adopted and published by the British

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 sodium 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. 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 400mg 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); and finally,
- Like fluoride, some of these substances (eg 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 (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 (permitted level) in micrograms per litre (µg/l)	% of permitted level added
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

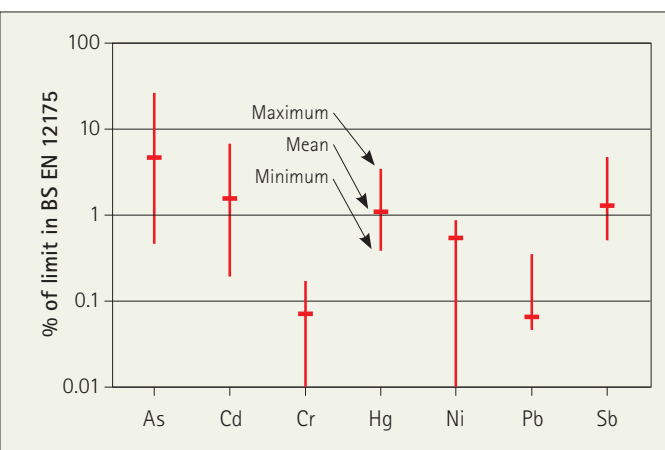
The maximum concentration of a contaminant that could be added to drinking water as a result of adding a fluoride dose of 1 ppm was calculated. These are shown in Tables 5 and 6, with the European permitted levels (Parametric Values) for comparison. Using arsenic and lead as examples, it can be seen 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).

Table 6 Impurities added by dosing sodium hexafluorosilicate (mg/kg is the same as parts per million, and micrograms per litre (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 (permitted level) in micrograms per litre (µg/l)	% of permitted level added
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

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 2000ⁱ. (The vast majority of fluoridation plants in the UK use hexafluorosilicic acid as the fluoridating agent.)

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 Organization as being safe for a lifetime's exposure (consumption of 2 litres of water per day over 70 years).

Conclusions

- 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 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.

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 been described in the previous section, European standards for water treatment chemicals under European Union 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

ⁱ Bob Hassall, Hydro Chemicals (UK) Limited, Personal Communication, June 2000.

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; they are important co-products of the manufacture of phosphate fertilisers. 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 above 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 involving 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 been discussed in detail in the previous section, 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 and 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 are minute, and become immeasurable when diluted thousands of times to achieve 1 part per million of fluoride



Fluorspar

Cryolite

Apatite

in water. Fluoridation therefore makes no measurable contribution to the concentration of these substances in the 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 fertilizers, and Fluorine for the manufacture of fluorides for water fluoridation is recovered from this process. The manufacturing process of 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 fertilizers as co-products of the manufacture of fluorosilicic acid, since each 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 USA. 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 compounds. ALCOA sold the chemical plant in the early 1950s; their last sales of sodium fluoride were in 1952ⁱ.

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.

Safety at the water treatment works

The Department of the Environment Code of Practice ensures that safety is the prime consideration when fluoride is added to water [6]. Water companies in the UK have almost 50 years experience in the successful operation of fluoridation schemes, and around the world there are thousands of highly successful fluoridation schemes in operation. In the United States alone – the country with the largest number of people drinking water with added fluoride – there are over 14,000 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 safetyⁱⁱ. 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 Plc
- United Utilities Water

ⁱ Source NIDR US Public Health Service 1993

ⁱⁱ The UK requirements for safety are considered to be among the most rigorous in the world (personal communication Tom Reeves, USPHS, CDC 5 May 2003.)

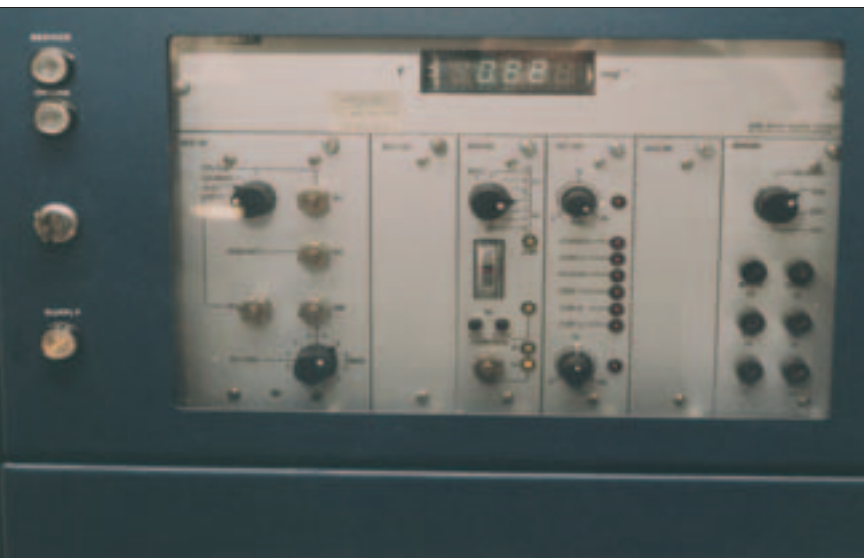
UK water suppliers that have in the past operated fluoridation schemes include:

- Department of the Environment for Ireland
- Thames Water
- Welsh Water
- Yorkshire Water

Code of practice

Strict operational criteria are laid down in the 1987 'Code of Practice on Technical Aspects of Fluoridation of Water Supplies' issued by the Department of the Environment [6]. These are designed to ensure that:

- The average fluoride content of the water leaving the treatment works in a calendar month is maintained between 0.9 and 1.1 parts per million, calculated for those periods when the fluoridation plant is in operation;



Fluoride monitor

- The fluoride content of the water leaving the treatment works is maintained between 0.8 and 1.2 parts per million for at least 90% of the time when the fluoridation plant is in operation; and,
- The fluoride content of the water leaving the treatment works shall not exceed 1.5 parts per million at any time.

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;



Day tank

- 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; and,
- f Regular servicing and maintenance.

What happens at the Water Treatment Works

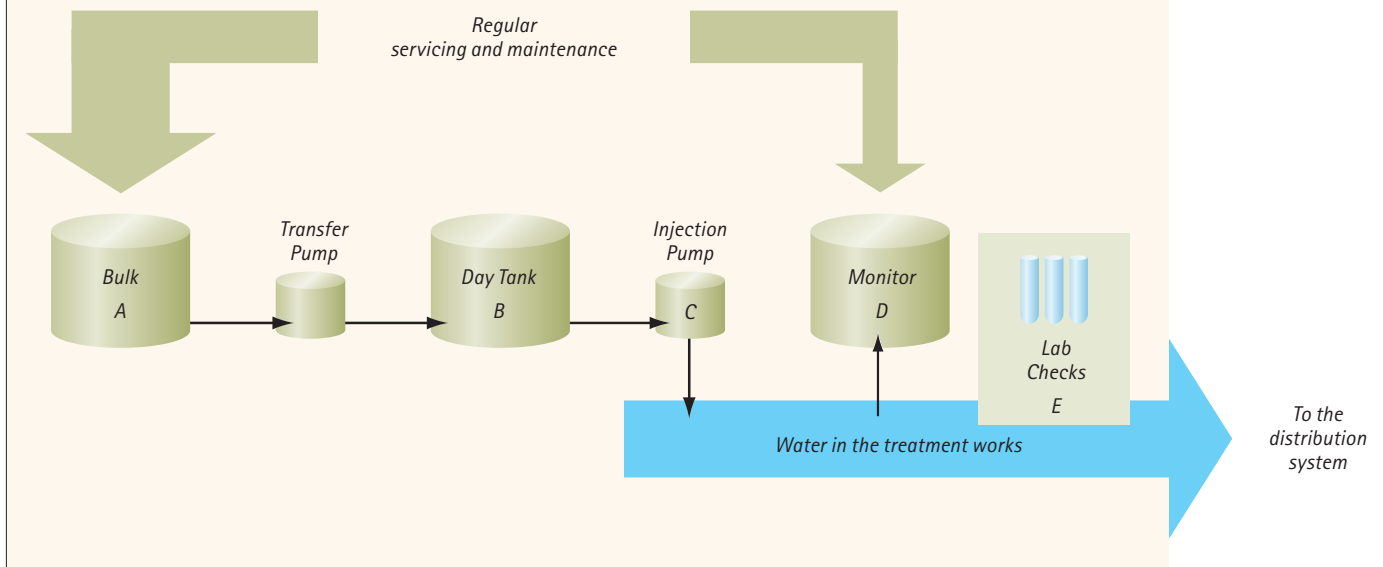
One day's supply at a time

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). 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

What happens at the Water Treatment Works



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) - 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. If at any time the fluoride level should exceed the permitted level, a warning is sounded in the control room and the whole plant is automatically shut down. The monitor itself also incorporates a fail-safe shut down of the fluoridation plant should the monitor or controller become 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]

Additional monitors and the need to update the code of practice

The safety features described above are *required*; all water companies operating fluoridation plant must comply, and the Drinking Water Inspectorate carries out regular checks on their performance in this respect.

In addition to the required safety arrangements described above, some water companies have installed additional monitors in their fluoridation plants. Water UK, the body that represents the whole of the UK water industry, has suggested that the Code of Practice should be reviewed and updated from time to time (see Water UK policy statement at the end of this section). The Code was originally published in 1987 and was prepared by a multidisciplinary working group of experts from the Department of the Environment, the water industry and the NHS. At the time of printing, the Drinking Water Inspectorate was leading a review of the 1987 Code; an updated 2004 edition was expected imminently.

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 the chemicals. Of course the water industry takes its Health and Safety responsibilities very seriously, and fortunately serious accidents involving water treatment chemicals are rare. Happily, since fluoridation began in the UK 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 USA. Since then hundreds of millions of people worldwide have regularly consumed fluoridated water – including nowadays around 350million, over 160 million of them in the USA.

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 USA 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. Such 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 assist them to develop and maintain standards of competence among their water plant operators.

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Water UK policy position on fluoridation of water supplies

Date: 5 July 2001

Updated September 2002

Current legislation is unsatisfactory. Decisions relating to fluoridation must be recognised as a health issue and statutory changes should be introduced to clarify policy and procedure on fluoridation for the water industry.

Water UK's aim is to ensure that:

- The present legislative position is recognised as unsatisfactory;
- If the Government wishes to promote fluoridation there should be a change through primary legislation such that
- If the Government, Health Authorities and customers so wish, water companies can be required to increase the fluoride content of the water they supply, and
- Companies' positions in respect of their operating arrangements, costs and indemnities are properly safeguarded.

Fluoride is a health issue

- Water operators have a primary duty to provide a sufficient and wholesome supply of water.
- The decision whether to fluoridate a water supply should be entirely a health issue. Health professionals are the only people in a position to make a decision about public health measures. The current discretion on water operators whether to accede to an application from a Health Authority should be removed.
- Water operators are contractors in the arrangement, who can be required to use the water supply network to deliver a product on behalf of the relevant local Health Authorities.

Decision-making

- There should be absolute clarity in the decision making process. The respective roles and responsibilities of the Health Authorities, national and local Government and water operators need to be spelled out.
- Whilst Health Authorities are the only bodies qualified to decide on the merits of fluoridation schemes we suggest that:
 - the decision making process must be absolutely clear;
 - the process should include improved provision for consulting with the population to be affected;
 - there should be a model consultation process agreed at the national level. Whilst the

water industry should have an input to the design of the model process, (which may also include local government) it should not play a part in the consultation itself;

- a parallel consultation between the Health Authority and water operator should take place, to ensure that fluoridation plant is installed to the required standards of the water operator;
- subject to the results of the consultation with the water operator the final decision should be taken by the Health Authority in public and in a transparent and understandable way;
- Health Authorities requiring fluoridation schemes should nevertheless be required to liaise with water operators to ensure that the present and future operations of the water operator are not compromised through the fluoridation of the water supply.

Public Relations

- The industry requires the support of public relations work led by Government and Health Authorities to make it absolutely clear who 'owns' (the Government, Health Authorities, or both) the issue of fluoridation.
- The industry's stance must remain neutral but it will provide information to customers and organisations as appropriate on the technical issues of fluoridating water supplies.
- The Health Authorities must take the lead in producing information on areas covered by fluoridation agreements and answering general enquiries and complaints from the public.

Indemnity

- Health Authorities must be responsible for all costs incurred by water operators as a consequence of the decision to implement a fluoridation scheme including:
 - costs of all works and plant required to fluoridate and the ongoing costs of operating and maintaining plant to nationally agreed standards and monitoring costs;
 - costs of management time and lost opportunity costs;
 - training of personnel, Health and Safety issues etc;
 - full legal indemnity - ie absolute indemnity on civil liability and indemnity on strict criminal liability as far as public policy allows;
 - in the event of bulk supply, common carriage or cross border supply the costs to de-fluoridate should also be recoverable;
 - supplying water to customers who

cannot for any valid reason drink water which is fluoridated

- the action of customers and others opposed to fluoridation (including the costs of debt recovery).
- The industry also requires an undertaking from the Department of Health and DETR to provide technical help to resist claims from customers, even though the Health Authorities are primary movers.
- Indemnities should remain, even if fluoridation proposals are withdrawn.

Maintaining operational flexibility

- Operators are increasingly integrating supply systems to maintain reliable and efficient operations. This makes it increasingly difficult to implement fluoridation on a piecemeal basis.
- Operators must maintain the flexibility to supply water from a particular source to different areas as the needs arise. This may entail suspension of fluoridation of supplies in some circumstances.
- Operators must be able to supply fluoridated water to normally non-fluoridated areas on the basis of operational contingencies without incurring any liability.
- The introduction of a fluoridation scheme must not operate as a barrier to development of competition in the water industry.
- Need a model agreement.

Code of Practice on technical aspects

- The industry needs to be confident that the Code of Practice on the Technical Aspects of Fluoridation of Water Supplies reflects best practice based on up-to-date knowledge.
- We suggest that the current code of practice be withdrawn and replaced by:
 - i) A DWI/WO/SO guidance letter setting out:
 - a) the roles of the different agencies and water operators
 - b) chemicals and specifications (linking to current drinking water regulation 25)

- c) dosage and allowable tolerances
- d) monitoring (validation and sampling regime over and above that required in the water quality regulations).

and

- ii) An industry code of practice setting out principles including:
 - a) a commitment to the highest operating levels and the use of failsafe equipment
 - b) storage and handling of chemicals
 - c) injection process
 - d) control of dose
 - e) monitoring
 - f) maintenance
 - g) reporting requirements to Health Authorities.
 - h) Health and Safety.