22 Technologies for fluoride removal

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22.1. Introduction

Fluoride is a normal constituent of natural water samples. Its concentration, though, varies significantly depending on the water source. Although both geological and man-made sources contribute to the occurrence of fluoride in water, the major contribution comes from geological resources. Except in isolated cases, surface waters seldom have fluoride levels exceeding 0.3 mg/l. Examples are streams flowing over granite rich in fluoride minerals and rivers that receive untreated fluoride-rich industrial wastewater. There are several fluoride bearing minerals in the earth's crust. They occur in sedimentary (limestone and sandstone) and igneous (granite) rocks. Weathering of these minerals along with volcanic and fumarolic processes lead to higher fluoride levels in groundwater. Dissolution of these barely soluble minerals depends on the water composition and the time of contact between the source minerals and the water.

Over the years groundwater has generally been considered to be a protected and safe source of water, fit for drinking without treatment, as the main focus has been on the bacteriological quality of potable water. Little consideration used to be given to the risks of chemical pollution, particularly to the presence of elevated levels of fluoride, arsenic and nitrate in groundwater. This chapter deals with only fluoride. Consumption of water having excess fluoride over a prolonged period leads to a chronic ailment known as fluorosis. Incidence of high-fluoride groundwater has been reported from 23 nations around the globe. It has led to endemic fluorosis, which has become a major geo-environmental health issue in many developing countries. According to a recent estimate, 62 million people are affected by various degrees of fluorosis in India alone (Susheela, 2001).

22.2. Health impacts of excess fluoride in potable waters

Low dental caries incidence rates demonstrate that fluoride concentrations of up to 1.0 mg/l in potable water are beneficial to the oral health of children and, to a lesser extent, adults. In several developed countries fluoridation of water supplies is practised if the natural concentration is below the desired level. Recently, however, fluoridation of drinking water has been questioned and many countries have expressed concerns over this practice due to the adverse health effects of fluoride.

Dental fluorosis, also called “mottled enamel”, occurs when the fluoride level in drinking water is marginally above 1.0 mg/l. A relationship between fluoride concentration in potable water and mottled enamel was first established in 1931. Typical manifestations of dental fluorosis are loss of shining and development of horizontal yellow streaks on teeth. Since this is caused by high fluoride in or adjacent to developing enamel, dental fluorosis develops in children born and brought up in endemic areas of fluorosis. Once formed, the changes in the enamel are permanent. When the above manifestations are seen in an adult, they clearly indicate that the person has been exposed to high fluoride levels during her or his childhood.

Skeletal fluorosis affects both adults and children and is generally manifested after consumption of water with fluoride levels exceeding 3 mg/l. Typical symptoms of skeletal fluorosis are pain in the joints and backbone. In severe cases this can result in crippling the patient. Recent studies have shown that excess intake of fluoride can also have certain non-skeletal health impacts such as gastro-intestinal problems, allergies, anaemia and urinary tract problems. Nutritional deficiencies can enhance the undesirable effects of fluoride.

22.3. Guidelines and standards

Taking health effects into consideration, the World Health Organization (1996) has set a guideline value of 1.5 mg/1 as the maximum permissible level of fluoride in drinking waters. However, it is important to consider climatic conditions, volume of water intake, diet and other factors in setting national standards for fluoride. As the fluoride intake determines health effects, standards are bound to be different for countries with temperate climates and for tropical countries, where significantly more water is consumed. Although water is generally the major route of fluoride intake, exposure from diet and air may become important in some situations. However, in many cases, the required data on different routes of exposure may be lacking. Data obtained by monitoring fluoride levels in local water supplies and the incidence of fluorosis in the local population can be used to arrive at the appropriate standards.

22.4. Fluoride control options

Search for alternative sources

If fluoride concentration in a community's water supply is significantly and consistently beyond the permissible level, it is essential to consider remedial measures to combat fluorosis. The first choice should be to search for water with a lower fluoride level. Options are:

(a) Provision of a new and alternate source of water with acceptable fluoride levels

It may be possible to get a safe water source in the vicinity by drilling a new well and/or drawing the water from different depths, as leaching of fluoride into groundwater is a localised phenomenon. Periodic monitoring is needed though, as mixing of water from different aquifers with different fluoride concentrations can occur.

(b) Transporting water from a distant source

This may lead to lasting benefits, but initial cost will be high. Such an approach has been implemented in endemic fluorosis areas in few countries.

(c) Blending high fluoride with low fluoride water

Mixing high and low fluoride waters so as to bring the concentration within permissible levels can be an appropriate long-term solution provided the low fluoride source is available within reasonable distance and is of acceptable quality with respect to other characteristics. This has been successfully implemented in the USA. Recently it has been tried in some parts of India.

(d) Dual water sources

If there are sources with both high and low fluoride levels available to the same community, the source having low fluoride levels can be strictly limited to drinking and cooking. The water source with high fluoride can then be used for other purposes. However, implementation of such dual supply systems requires extensive community awareness programmes. The use of different sources for different purposes may also be hampered by socio-economic factors such as greater distances and burdens of water collection and having to share water sources with users from other neighbourhoods. Education alone is often insufficient to change practices, especially since the impact comes only after prolonged use of high fluoride water sources. Cost of a piped water supply system will be almost doubled when water with low and high fluoride content is supplied through parallel systems. Low-fluoride water could also be sold in containers via commercial outlets.

(e) Rainwater harvesting

There are two ways in which rainwater harvesting (see chapter 7) can be used as a solution for the fluoride problem. Individual household-roof rainwater harvesting and container storage can provide potable water for families. Or harvested surface water run-off can be used to recharge high-fluoride groundwater sources.

Presenting these options with their implications, advantages and disadvantages to community leaders and male and female heads of households will help these groups to make informed choices on the most appropriate solutions in their particular situation.

Defluoridation of water

When none of the above options is feasible or if the only solution would take a long time for planning and implementation, defluoridation of drinking water has to be practised. Two options are then available: (i) the central treatment of water at the source and (ii) the treatment of water at the point of use that is, at the household level. In developed countries treatment at the source is the method adopted. Defluoridation is carried out on a large scale under the supervision of skilled personnel, usually at a treatment works alongside other treatment processes. Cost is not then a limiting factor. The same approach may not be feasible in less developed countries, especially in rural areas, where settlements are scattered. Treatment may only be possible at a decentralised level, i.e. at the community, village or household level. Treatment at the point of use has several advantages over treatment at community level. Costs are lower, as defluoridation can be restricted to the demand for cooking and drinking – usually less than 25% of the total water demand. Chemical treatment of the entire water demand would lead to production of large volumes of sludge, which requires a safe disposal.

Limitations of point of use treatment are that reliability of the treatment units has to be assured, and that all users should be motivated to use only the treated water for drinking and cooking when untreated water is also available in the house.

Defluoridation methods can be broadly divided into three categories according to the main removal mechanism:

- Chemical additive methods
- Contact precipitation
- Adsorption/ion exchange methods

Chemical additive methods

These methods involve the addition of soluble chemicals to the water. Fluoride is removed either by precipitation, co-precipitation, or adsorption onto the formed precipitate. Chemicals include lime used alone or with magnesium or aluminium salts along with coagulant aids. Treatment with lime and magnesium makes the water unsuitable for drinking because of the high pH after treatment. The use of alum and a small amount of lime has been extensively studied for defluoridation of drinking water. The method is popularly known as the *Nalgonda technique* (RENDWM, 1993), named after the town in India where it was first used at water works level. It involves adding lime (5% of alum), bleaching powder (optional) and alum ($Al_2(SO_4)_3.18H_2O$) in sequence to the water, followed by coagulation, sedimentation and filtration. A much larger dose of alum is required for fluoride removal (150 mg/mg F-), compared with the doses used in routine water treatment.

As hydrolysis of alum to aluminium hydroxide releases H^+ ions, lime is added to maintain the neutral pH in the treated water. Excess lime is used to hasten sludge settling. The dosage of alum and lime to be added to raw waters with different initial fluoride concentrations and alkalinity levels is given in table 22.1.

Table 22.1 Approximate volume of 10% alum solution (ml) to be added in 40 litres of test water to obtain the acceptable limit (1.0 mg F/l) of fluoride at various alkalinity and fluoride levels. The lime to be added is 5% of the alum amount (mg/l)

Test water fluorides (mg/l)	Test water alkalinity as mg $CaCO_3$/l							
	125	200	300	400	500	600	800	1000
2	60	90	110	125	140	160	190	210
3	90	120	140	160	205	210	235	310
4		60	165	190	225	240	275	375
5			205	240	275	290	355	405
6			245	285	315	375	425	485
8					395	450	520	570
10							605	675

(Adapted from RGNDWM, 1993)

The Nalgonda technique has been successfully used at both individual and community levels in India and other developing countries like China and Tanzania. Domestic defluoridation units are designed for the treatment of 40 litres of water (Fig. 22.1) whereas the fill-and-draw defluoridation plant (Fig. 22.2) can be used for small communities. Alum treatment is seldom used for defluoridation of drinking water in developed countries.

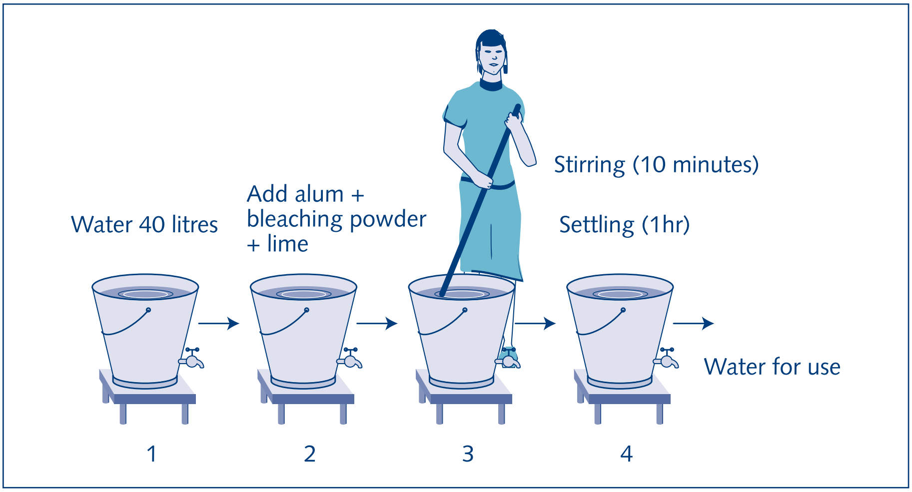

Figure 22.1. Home-based defluoridation using Nalgonda technology (Adapted from RDNDWM, 1993)

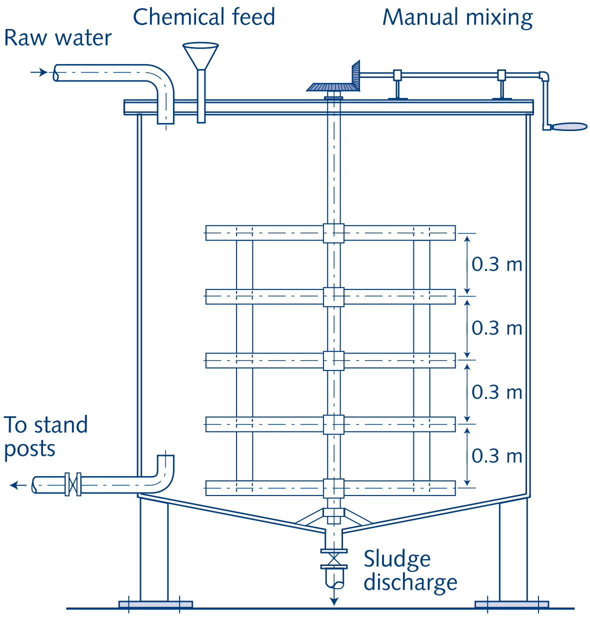

Figure 22.2. Fill-and-draw defluoridation plant for small community (Adapted from RDNDWM, 1993)

Contact Precipitation

Contact precipitation is a recently reported technique in which fluoride is removed from water through the addition of calcium and phosphate compounds. The presence of a saturated bone charcoal medium acts as a catalyst for the precipitation of fluoride either as CaF_2, and/or fluorapatite (Fig. 22.3). Tests at community level in Tanzania have shown promising results of high efficiency. Reliability, good water quality and low cost are reported advantages of this method (Chilton, et al., 1999).

Adsorption/ion-exchange method

In the adsorption method, raw water is passed through a bed containing defluoridating material. The material retains fluoride either by physical, chemical or ion exchange mechanisms. The adsorbent gets saturated after a period of operation and requires regeneration.

A wide range of materials has been tried for fluoride uptake. Bauxite, magnetite, kaolinite, serpentine, various types of clays and red mud are some of the naturally occurring materials studied. The general mechanism of fluoride uptake by these materials is the exchange of metal lattice hydroxyl or other anionic groups with fluoride. Fluoride uptake capacity can be increased by certain pre-treatments like acid washing, calcinations, etc. None of the mentioned materials generally exhibits high fluoride uptake capacities.

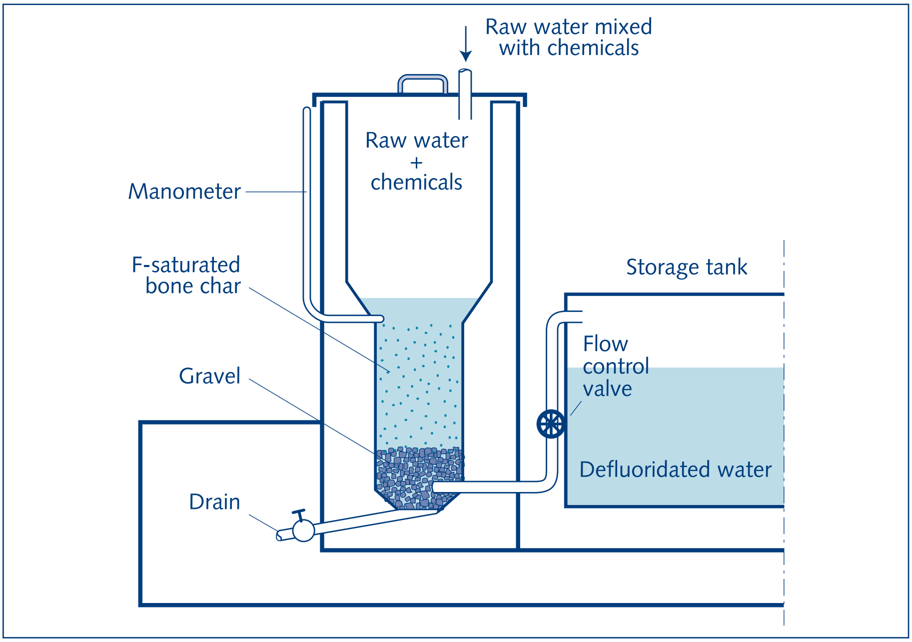

Fig. 22.3. Contact precipitation for fluoride removal (design used in Tanzania)
Source: Bailey K., et al., 1999

Processed materials like activated alumina, activated carbon, bone char, defluoron-2 (sulphonated coal) and synthetic materials like ion exchange resins have been extensively evaluated for defluoridation of drinking water. Among these materials, bone char, activated alumina and calcined clays have been successfully used in the field; (Cummins, 1985, Susannae Rajchagool and Chaiyan Rajchagool, 1997; and Priyanta and Padamasiri, 1996). Application of these materials is described below.

Bone char as a defluoridating material. Bone char consists of ground animal bones that have been charred to remove all organic matter. Major components of bone charcoal are calcium phosphate, calcium carbonate and activated carbon. The fluoride removal mechanism involves the replacement of carbonate of bone char by fluoride ion. The method of preparation of bone charcoal is crucial for its fluoride uptake capacity and the treated water quality. Poor quality bone char can impart bad taste and odour to water. Exhausted bone char is regenerated using caustic soda. Since acid dissolves bone char, extreme care has to taken for neutralising caustic soda. Presence of arsenic in water interferes with fluoride removal.

In the USA in the past, a few defluoridation plants were using bone char. Now they have been largely replaced by activated alumina. Bone char is considered as an appropriate defluoridating material in some developing countries. The ICOH[1] domestic

1 ICOH = Inter-Country Centre for Oral Health at the University of Chiong Mai, Thailand

defluoridator was developed in Thailand and uses crushed charcoal and bone char (Fig. 22.4). Its defluoridation efficiency depends on the fluoride concentration in raw water as well as the fluoride uptake capacity and the amount of bone char used in the filter. Field trials in Thailand, Sri Lanka and some African countries have shown very encouraging results (Priyanta and Padamasiri, 1996; Mjengera et al., 1997; and Susannae Rajchagool and Chaiyan Rajchagool, 1997). Reports from Sri Lanka have shown that with 300 gm charcoal (mainly to remove colour and odour) and 1 kg bone char an ICOH filter can defluoridate on an average 450 litres of water containing 5 mg/l F- at a flow rate of 4 litres per hour. Regeneration of spent bone char is not recommended for these household units. Instead it should be replaced with fresh material commercially available in local shops.

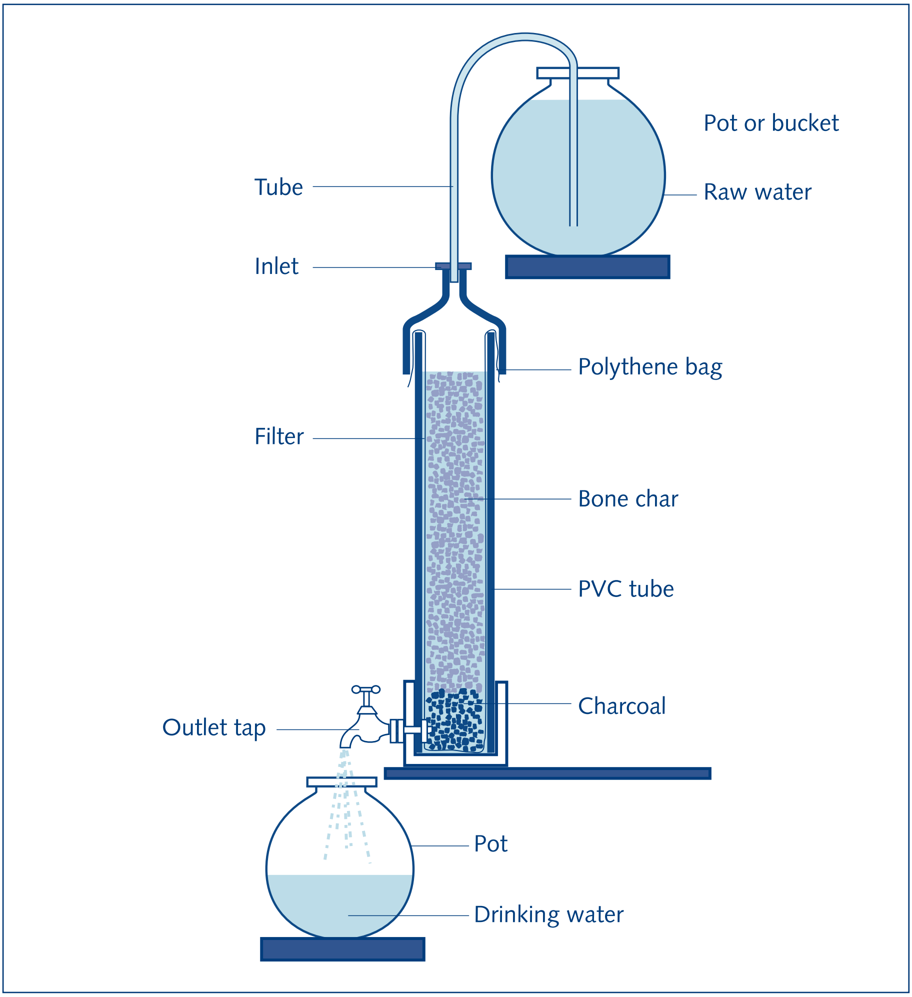

Figure 22.4. Bone char domestic defluoridator developed by ICOH-Thailand

Activated alumina as a defluoridating material. Activated alumina or calcined alumina, is aluminium oxide, Al2O3. It is prepared by low temperature dehydration (300-600°C) of aluminium hydroxides. Activated alumina has been used for defluoridation of drinking water since 1934, just after excess fluoride in water was identified as the cause of fluorosis.

The fluoride uptake capacity of activated alumina depends on the specific grade of activated alumina, the particle size and the water chemistry (pH, alkalinity and fluoride concentrations). In large community plants the pH of the raw water is brought down to 5.5 before defluoridation, as this pH has been found to be optimum and it eliminates bicarbonate interference. The mechanism of fluoride removal is most probably the ligand exchange reaction at the surface of activated alumina. Exhausted activated alumina has to be regenerated using caustic soda. To restore the fluoride removal capacity, basic alumina is acidified by bringing it into contact with an excess of dilute acid (Clifford, 1990).

Activated alumina has been the method of choice for defluoridation of drinking water in developed countries. Generally it is implemented on a large scale in point of source community plants. A few point of use defluoridation units have been developed which can be directly attached to the tap. During recent years this technology is gaining wide attention even in developing countries. Domestic defluoridation units (Fig. 22.5) have been developed in India using indigenously manufactured activated alumina, which is commercially available in bulk quantities. Choosing the proper grade of activated alumina is important for its effective reuse in multiple defluoridation cycles. Around 500-1500 litres of safe water could be produced with 3 kg of activated alumina when the raw water fluoride is 11 and 4 mg/l respectively at natural water pH of 7.8-8.2. The frequency of regeneration is once in 1.5-3 months. The cost of activated alumina is around US$ 2 per kg and the total cost of the domestic filter depends upon material used for filter assembly. Regeneration of exhausted activated alumina costs around US$ 0.5 (Venkobachar et al., 1997).

Major requirements are the creation of demand for treatment and the setting up of good supply and financing systems and arrangements for regeneration. Sale of the ingredients and the provision of education and monitoring through visits to user households has in some places become a source of income for trained women promoters. The units are being evaluated in several villages in India. Daily operational care for using these units is normally negligible. However, the exhausted activated alumina has to be regenerated once every few months. This is carried out at the village level.

Calcined clay. Freshly fired brick pieces are used in Sri Lanka for the removal of fluoride in domestic defluoridation units (Fig. 22.6). The brick bed in the unit is layered on the top with charred coconut shells and pebbles. Water is passed through the unit in an upflow mode. The performance of domestic units has been evaluated in rural areas of

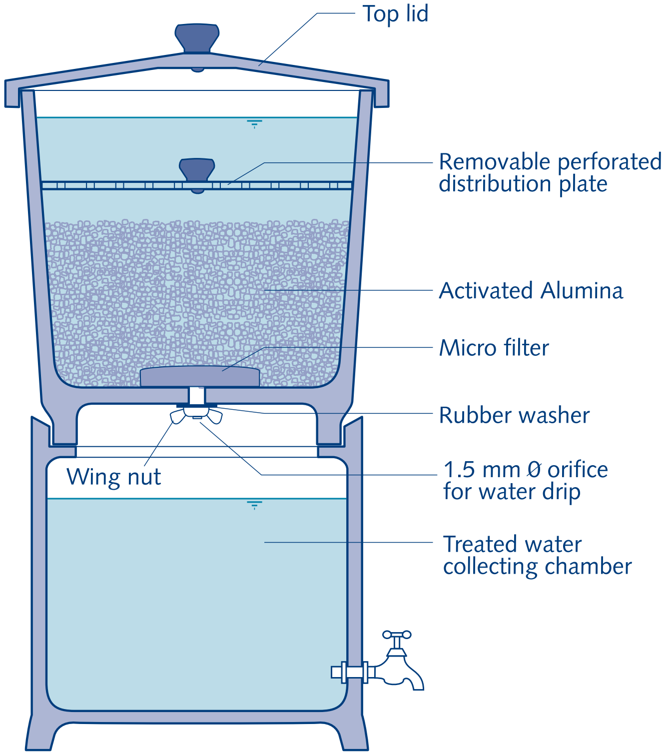

Fig. 22.5. Activated alumina-based domestic defluoridation filter

Sri Lanka (Priyanta & Padamsiri 1997). It is reported that efficiency depends on the quality of the freshly burnt bricks. The unit could be used for 25-40 days, when withdrawal of defluoridated water per day was around 8 litres and raw water fluoride concentration was 5 mg/l. As PVC pipes are costly, a defluoridator made out of cement and bricks has also been recommended. Apart from the methods discussed above, specific synthetic ion exchangers and separation technologies such as reverse osmosis and electrodialysis have also been developed for fluoride removal from potable water.

To select a suitable defluoridation method for application in developing countries, some of the following criteria need to be considered:

- Fluoride removal capacity
- Simple design
- Easy availability of required materials and chemicals
- Acceptability of the method by users with respect to taste and cost

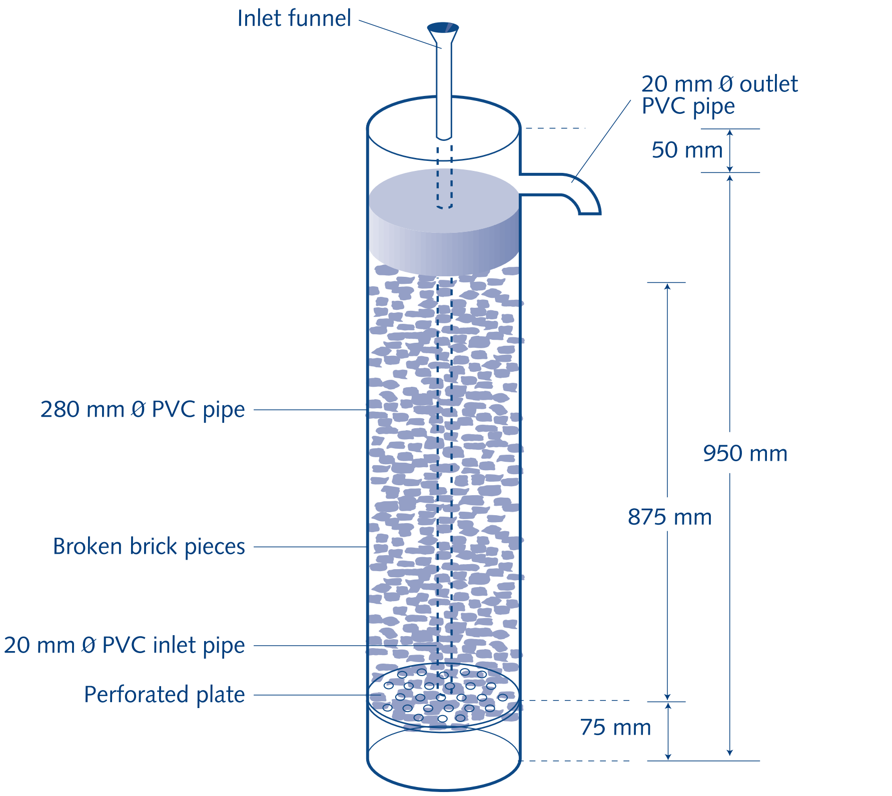

Fig. 22.6. Domestic defluoridation unit using brick pieces
Source: Priyanta and Padamasiri, 1996

Both precipitation and adsorption methods have advantages and limitations. In the Nalgonda technique easily available chemicals are used and the method is economically attractive. Limitations of the method are varying alum doses depending on fluoride levels in water, daily addition of chemicals and stirring for 10-15 min, which many users may find difficult. In adsorption-based methods like activated alumina and bone char, daily operation is negligible. Activated alumina is costly. Hence exhausted alumina has to be regenerated using caustic soda and acid and repeatedly reused, at least for a few cycles. Improperly prepared bone char imparts taste and odour to the treated water. Since bone char from point of use units is not generally regenerated, a ready supply of properly prepared material needs to be available. Furthermore, bone char may not be culturally acceptable to certain communities as defluoridating material. Some of the merits and demerits of defluoridation methods are given in table 22.2.

Table 22.2 Merits and demerits of some defluoridation methods

Method	Capacity	Working pH	Merits	Demerits	Estimated relative cost
Nalgonda	150 mg alum dose / mg F^- removal; dose varies with alkalinity	Ambient	Low technology; adaptable at point of use & point of source level	• Large quantities of sludge • High chemical dose • Dose depending on F- level • Daily addition of chemicals and stirring in point of source units	Low-medium
Bone char	Variable design value 1000-2000 mg/kg	Ambient	Locally available media	• May impart taste and odour and result in organic leaching if not prepared properly • Requires regeneration periodically • Affected by high alkalinity • May not be acceptable in some countries	Low-medium
Activated alumina	Variable 1000-1500 mg/kg	5-6 in large defluoridation plants; ambient in point of use units	Effective; much experience	• Periodic regeneration • Skilled personnel for plant operation • Properly trained staff for regeneration of point of use units • Suitable grades may not be indigenously available in less developed countries	Medium-high
Contact precipitation	No information	Ambient	Not much experience	• Algal growth can occur in phosphate solution. • Bone char used as a catalyst may not be acceptable in many countries	High-very high
Brick	No information	Ambient	Low-cost technology	• May not be universally applicable	High-very high
Reverse osmosis/ electrodialysis	High	Ambient	Can remove other ions	• Skilled operation • Interference by turbidity • High cost	Very high

Bibliography

Bailey K. et al. (1999). *Fluoride in drinking water.* Geneva, Switzerland, World Health Organization.

Clifford, D.A (1990). 'Ion exchange and inorganic adsorption in water quality and treatment'. In: *Pontius, F.W. (ed.). A handbook of community water supplies.* 4th ed. New York, NY, USA, McGraw Hill.

Cummins, B.T. (1985). *Controlling fluoride levels: a literature review.* Geneva, Switzerland, World Health Organization.

Mjengera, H.J.; Mtalo, F.W.; Mashauri D.A. and Tjell, C.H. (1997). 'Fluoride removal using heat activated animal bone media.' In: *Dahi, E. and Nielsen, J.M. (eds). Proceedings of the 2nd international workshop on fluorosis and defluoridation of water, Addis Ababa, Ethiopia, November 19-22, 1997.* Dunedin, New Zealand, International Society for Fluoride Research.

Priyantha, N. and Padamasiri, J.P. (eds). (1996). *Proceedings: prevention of fluorosis in Sri Lanka.* Peradeniya, Sri Lanka, University of Peradeniya.

Rajchagool, S and Rajchagool, C. (1997). 'Solving the fluorosis problem in a developing country'. In: *Dahi, E. and Nielsen, J.M. (eds). Proceedings of the 2nd international workshop on fluorosis and defluoridation of water, Addis Ababa, Ethiopia, November 19-22, 1997.* Dunedin, New Zealand, International Society for Fluoride Research.

RGNDWM (1993). *Prevention and control of fluorosis. Vol. II. Water quality and defluoridation techniques.* New Delhi, India, Rajiv Gandhi National Drinking Water Mission.

Susheela, A.K. (2001). *A treatise on fluorosis.* New Delhi, India, Fluorosis Research and Rural Development Foundation.

Venkobachar, C.; Iyengar, L. and Mudgal, A. (1997). 'Household defluoridation of drinking water using activated alumina technology'. In: *Dahi, E. and Nielsen, J.M. (eds). Proceedings of the 2nd international workshop on fluorosis and defluoridation of water, Addis Ababa, Ethiopia, November 19-22, 1997.* Dunedin, New Zealand, International Society for Fluoride Research.

WHO -Geneva, CH (1996). *Guidelines for drinking-water quality. Vol. 2. Health criteria and other supporting information.* 2nd ed. Geneva, Switzerland, World Health Organization. http://www.who.int/water_sanitation_health/GDWQ/GWDWQindex.html

Web sites

Fluorosis: http://www.education.vsnl.com/fluorosis

Voice: http://www.voice.buz.org/fluoridation

No Fluoride: http://www.nofluoride.com

Inter country Centre for Oral Health: http://www.icoh.org

UNICEF: http://www.unicef.org