Contact precipitation for defluoridation of water
[Discussion paper]

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In spite of the fact that millions of people in developing countries are suffering from fluorosis, mainly due to the high fluoride concentrations in their drinking water, no method of defluoridation of water has been reported to be carried out successfully as a routine in any of these countries so far. This is quite remarkable, especially when taking into consideration that several defluoridation methods have been studied in details and even reported as appropriate methods, for quite a number of years (Bulusu et al. 1979).

This oddity is probably due to the fact that the available defluoridation methods do have disadvantages. Some of these are what may be designated as killer disadvantages, in the sense that the method turn out to be unsustainable under the given socioeconomical conditions. As killer disadvantages of defluoridation methods could be mentioned:

- **High Cost-Tech:** i.e. either the price and/or the technology is high, demanding imported spare parts, continuous power supply, expensive chemicals, skilled operation or regeneration and the like. Reverse osmosis, ion exchange and activated alumina may thus be categorised as high cost-tech methods.
- **Limited efficiency:** i.e. the method does not imply sufficient removal of the fluoride, even when appropriate dosage is used. Like in the Nalgonda technique, the residual concentration is mostly higher than 1 mg/l.
- **Unnoticeable break through:** i.e. the fluoride concentration in the treated water may rise gradually or suddenly typically when a medium in a treatment column is exhausted or even when the flow is out of control. Like in the case of bone char and other column filters, these techniques necessitate continuous monitoring of fluoride residual, or at least the rate and the volume of treated water, if the unnoticeable break through or the waste of removal capacity are to be avoided.
- **Limited capacity:** while the removal capacity of bone char or activated alumina may be about 2 mg fluoride per g of medium, much higher amounts of f. ex. calcined clay or Nirmali seeds, has to be used in order to obtain appropriate removal.
- **Deteriorated water quality:** some methods like the activated magnesia would by nature result in too high pH-values, normally above 10. The water quality may also deteriorate due to poorly prepared medium (bone char) or due to medium escaping the treatment container, e.g. ion exchange, alumina, Nalgonda sludge etc.
- **Taboo limitations:** especially the bone char method is culturally not acceptable to Hindus. The bone char origin from pigs may be questioned by Muslims. Even the charring of bones have been reported to be repulsive to villages in North Thailand.

The paper reports a new water defluoridation method, developed in Denmark and tested in Tanzania at village school level, apparently without most of the above mentioned killer disadvantages.

**Experimental setup**

**Plant description**

Figure 1 shows the contact precipitation plant as developed and installed at the Ngurdoto school in Ngurdoto Village, the Arusha Region, Northern Tanzania. The plant consists of a contact column, containing a relatively small contact bed, above which a relatively large supernatant space is left as a raw water column, in which the chemicals are mixed. The filter bed contains bone char which is already saturated with respect to the fluoride in the raw water. Gravel is used as bearing medium. From here the defluoridated water is withdrawn continuously by gravity to a low but wide defluoridated water tank. The defluoridated water tank is connected at the bottom, through a wall (not shown in figure 1) to a tap outside the operation room in the school yard. The connection pipe between the bottom of the contact column and the defluoridated water tank is supplied with a flow control valve in order to control the minimum contact time in the raw water compartment and in the contact bed. Both the contact column and the defluoridated water tank are supplied with plastic tubes used as manometers. Both tubes are ended few cm below the upper edges of the tanks in order eventually to unveil overflow. As pressured raw water is not available, the plant is provided with a hand pump and a bucket in order to make it easy for the care taker to add the stock solutions and the raw water at ground level.

**Plant operation**

The water is fetched in buckets from a stand post near by to the operation room by school pupils volunteers. Initially the raw water column would be empty. The plant care taker starts closing the flow control valve in order to control the minimum contact time in the raw water compartment and in the contact bed. Both the contact column and the defluoridated water tank are supplied with plastic tubes used as manometers. Both tubes are ended few cm below the upper edges of the tanks in order eventually to unveil overflow. As pressured raw water is not available, the plant is provided with a hand pump and a bucket in order to make it easy for the care taker to add the stock solutions and the raw water at ground level.
raw waters in the first two buckets. The remaining water is then pumped to fill the raw water column, in total about seven buckets. As raw water is falling into the raw water column, the supernatant water is completely mixed. The flow control valve is then opened, but only to allow slow flow through the contact bed, the average filtration velocity not exceeding 1 m/h. A water sample is taken by the plant keeper for testing. This procedure is carried out once a day, apart from holidays. However, in between, the procedure is omitted or carried out twice in the same day in order to keep the defluoridated water available, without wasting any of it.

Stock solutions
The two stock solutions are prepared by the caretaker once every 10th operation day. Two special measuring cups are used for volumetric portioning of the chemicals, respectively 150 g of Sodiumdihydrogenphosphate (142 ml MSP) and 300 g of calcium chloride (311 ml CC). The chemicals used are both from the Swedish Kemira LTD. MSP is fabricated as Bolifor Granuler containing 24 per cent P and 20 per cent Na. CC is fabricated as technical grade flakes containing 77-80 per cent calcium chloride. The chemicals are dissolved each separately in 15 l defluoridated water. The stock solutions containers along with the respective chemical bags and the measuring cups and cylinders are coloured respectively in red and green in order to minimise the possibility of failure dosage.

Fluoride measurements
The fluoride concentrations were measured using a Metrohm fluoride electrode and a Metrohm Ag/AgCl reference electrode with a sleeve type diaphragm con-

Figure 1. The contact precipitation plant as designed and operated, so far for one year at the Ngurdoto Village primary school, the Arusha Region, Northern Tanzania
Table 1. Plant and operation characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total contact column depth</td>
<td>1.7 m</td>
</tr>
<tr>
<td>Inner diameter of contact column</td>
<td>0.32 m</td>
</tr>
<tr>
<td>Supernatant Raw water column depth</td>
<td>1.1 m</td>
</tr>
<tr>
<td>Saturated bone char bed depth</td>
<td>0.28 m</td>
</tr>
<tr>
<td>Gravel depth</td>
<td>0.25 m</td>
</tr>
<tr>
<td>Defluoridated water tank depth</td>
<td>0.5 m</td>
</tr>
<tr>
<td>Defluoridated water tank diameter</td>
<td>1 m</td>
</tr>
<tr>
<td>Bone char porosity</td>
<td>0.56</td>
</tr>
<tr>
<td>Bone char bulk density</td>
<td>0.83 kg/l</td>
</tr>
<tr>
<td>Bone char grain size</td>
<td>1.4 mm</td>
</tr>
<tr>
<td>Flow time (100 l)</td>
<td>58 - 65 min</td>
</tr>
<tr>
<td>Utilised capacity (weekend excluded)</td>
<td>100 l/day</td>
</tr>
</tbody>
</table>

Results
The above mentioned plant has been operated about one year, from 6th October 1995 and up to now, apart from minor interruptions during holidays. During this period the contents of fluoride in the raw water was subject to seasonal and maybe other variations, between 8.2 and 13mg/l. The effluent concentration was 0.9mg F/l in the very first day, but otherwise about 0.5 falling down to about 0.05. Thus the average removal efficiency during this first year of operation being 97.9 per cent.

White precipitate was accumulating as a sludge blanket on the top layer of the saturated bone char. However this seemed not to affect the effluent water quality nor the time required for the raw water to pass through the filter. This was measured to be between 58 and 65 minutes, indicating an average surface loading of about 1m/h.

Discussion
The process of contact precipitation was discovered by studying some of the laboratory results, where bone char was supposed to be regenerated according to a “surface coating” procedure published by Christoffersen et al. 1991. The mechanisms of contact precipitation are not fully understood, but it has been proved that the process can not take place, at least not immediately as described above, if sand, marble, bone ash, or activated carbon is

Table 2. Estimated running costs for chemicals purchased in large quantities in Europe

Transportation and equipment costs are not considered. The unit price and the residual fluoride concentration are estimated for 10 mg/l initial fluoride concentration.

<table>
<thead>
<tr>
<th>Treatment Method</th>
<th>Chemical Used</th>
<th>Formula</th>
<th>Price* US$/ton</th>
<th>Dosage g/m³</th>
<th>Residual Conc. mg/l F⁻</th>
<th>Unit Price US$/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nalgonda</td>
<td>Aluminium Sulphate</td>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>468</td>
<td>812</td>
<td>2.0</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Calcium Oxide (Lime)</td>
<td>CaO</td>
<td>283</td>
<td>219</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bone Char**</td>
<td></td>
<td></td>
<td>333</td>
<td>2300</td>
<td>0.8</td>
<td>0.76</td>
</tr>
<tr>
<td>Contact Precipitation</td>
<td>Calcium Chloride (CC)</td>
<td>CaCl₂·2H₂O</td>
<td>283</td>
<td>333</td>
<td>0.4</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Sodium Dihydrogen</td>
<td>NaH₂PO₄·H₂O</td>
<td>780</td>
<td>167</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phosphate (MSP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Amount of 10 tons or more, purchased from Kemira LTD, in Sweden.
** The given price for bone char is from China.
Bone char from UK and Tanzania apparently cost much different, 2280 and 167 US$ /Ton respectively.
The fluoride removal capacity of bone char is assumed to be high; 4 mg/g.
used instead of the saturated bone char (data to be published). On the other hand the saturated bone char cannot remove any fluoride if the chemicals MSP and CC are not added. Naturally it may be thought that the bone char is acting as a catalyst of the precipitation plus of course the filtration of the precipitate, which most probably would consist of fluorapatite. However, looking at the stoichiometry of the removal, the process, at least at the employed relatively high initial fluoride concentration, may involve some precipitation of calcium fluoride and probably calcium hydrogen phosphate as well. The reason being that up to two litres of the stock solutions would have been required, if all the removed fluoride was precipitated as pure fluorapatite. It must be added that the dosage of chemicals, and the its design criteria, are still to be optimised and derived.

Similarly, it is not known, how long time this operation could be continued before a break through, or, more likely, the filter bed is clogged. If the precipitated chemicals are assumed to have a net density of about 3.2 kg/l, and if they are cumulated in the pores of the bone char, it would only replace about 13 per cent of the pore water in the bed compartment. This is probably the explanation behind the fact that the head loss of the contact filter was almost unchanged, even after one year of plant operation. On the other hand it may be expected that the plant, sooner or later, would need back washing. Experiences on this are yet to be gained.

The socioeconomy of the process is also still to be elaborated on. However, assuming that the prices of the chemicals would be most significant, a rough comparison is made between the price of MSP + CC in the contact precipitation process and the chemicals in Nalgonda technique and in the simple bone char sorption process. The unit prices used are selected purchase in Europe at an appropriate tonnage, table 2. These preliminary estimates indicate, that the chemical price for contact precipitation may be half as much as chemical price in the Nalgonda process, which is already well known to be the cheapest defluoridation process (Bulusu et al. 1979). Moreover, the chemical price in the contact precipitation process may be one fourth of the chemical price in the bone char process, which is already known to be the preferred defluoridation method in Thailand.

When taking into consideration the disadvantages of high fluoride residual in the Nalgonda process, and the problems of monitoring and break through in the bone char process, it may be concluded that the contact precipitation process seems to be the most promising defluoridation method ever tested at village level in a developing country.

References


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