

Defluoridation of water using Activated Alumina Technology: Studies carried out at IIT Kanpur*

1. BACKGROUND

Groundwater has become a source of drinking water since last few decades, due to the scarcity, non-availability and bacteriological pollution of surface waters in many developing and underdeveloped countries. Millions of handpumps and deep tubewells have been installed in India since 1970, to provide safe drinking water to rural population, as groundwater is generally free of bacteriological contamination. Although this drastically reduced the incidence of water borne diseases, it has led to the emergence of chronic health effects in many parts of the country due to the excessive presence of chemical constituents like fluoride and arsenic in groundwater in some parts of the country. These have become major geo-environmental issues (1, 2). Not much attention was given in the initial stages to the presence of these chemical constituents, as clinical manifestations appear after a prolonged intake of contaminated water.

Fluoride is a normal constituent of natural waters. Its concentration, however, varies depending on the water source. Surface waters seldom have fluoride concentrations beyond 0.3mg/L, except in isolated cases. Weathering of fluoride bearing minerals, volcanic and fumarolic processes as well as hydrogeological conditions can lead to higher fluoride levels in groundwater in certain areas, which become endemic for fluorosis.

It is essential to consider remedial measures to control fluorosis, if fluoride levels of potable water are consistently beyond permissible levels. One possibility is to search for a safe water source locally or transport from a distant safe source through a piped water supply system. Another emerging option is rain water harvesting. Defluoridation of water should be considered only, where other options are not feasible or as an interim measure, if the other options take a long time for planning and implementation.

Defluoridation methods can be broadly divided into following categories (3).

1. Chemical addition/precipitation
2. Adsorption/ion exchange
3. Membrane based technologies.

Each of these methods has its own merits and limitations.

By mid 1980's, it was evident that excess fluoride was present in groundwaters in many parts of the country. In 1987, Rajiv Gandhi National Drinking Water Mission estimated that about 25 million people in 8700 villages were drinking water with excess fluoride. As per recent estimates, this figure has been quoted to be 62 million (2). A Sub-Mission to control fluorosis was set up with a plan to overcome the problem. Testing of all water sources for fluoride and technology interventions were initiated in many states, Technology option considered was mainly Nalgonda technique.

* Prepared by Dr. Lela Iyenger, Indian Institute of Technology, Kanpur in March 2005, for UNICEF, New Delhi

NEERI scientists had developed "Nalgonda Technique" for the defluoridation of drinking water. This involved the addition of alum and lime to water, followed by settling and filtration. The first report on this method was published in 1975. Based on this technology, community level (fill and draw type), handpump attachable and domestic defluoridation units were developed. Many community and hand pump defluoridation units were installed in various states. Pilot studies on domestic defluoridation units were also initiated.

Activated Alumina (AA) technology is one of the widely used adsorption/ ion exchange methods for the defluoridation of potable water and many reports are available on large-scale installations (4, 5). Defluoridation in such units is carried out under supervision of skilled personnel and treated water is supplied to townships. The quality of treated water from such facilities is assured. However, this approach is not immediately feasible in developing countries, especially in rural areas. Treatment may only be possible at a community level i.e. handpump installations or at the 'point of use', i.e. domestic level. Reports on the adaptation of AA technology at handpump or home units were scarce till 1990's as this technology was rarely used in developing countries.

During 1980-1990, use of indigenously manufactured activated alumina for fluoride removal was reported by few laboratories, including IIT Kanpur. Activated Alumina manufactured by Associated Cement Company and Indian PetroChemicals Ltd. (IPCL.) were used in most of these studies (6, 7). Venkateswara Rao and Mahajan (8) reported the development and evaluation of domestic and handpump units where activated alumina was used as the defluoridation medium. Kartikeyan et. al. (9) screened three different grades of activated alumina (particle size, < 0.4 mm) for fluoride uptake capacity as well as designed and evaluated domestic defluoridation unit.

Studies carried out on defluoridation of drinking water at IIT Kanpur since 1991, using AA technology, are presented briefly in this report. Financial assistance from UNICEF during this entire period is gratefully acknowledged.

2. MAJOR AREAS OF STUDY:

The initial intention of the research project in 1993 was to develop and field test a handpump based defluoridation unit that could be maintained by local communities. Around 1996, the focus of the research changed to finding solutions for domestic defluoridation. At the same time, the discontinuation of the grade of AA used (manufactured by IPCL) during 1991-96, led to the screening of other grades indigenously manufactured of activated alumina for defluoridation application.

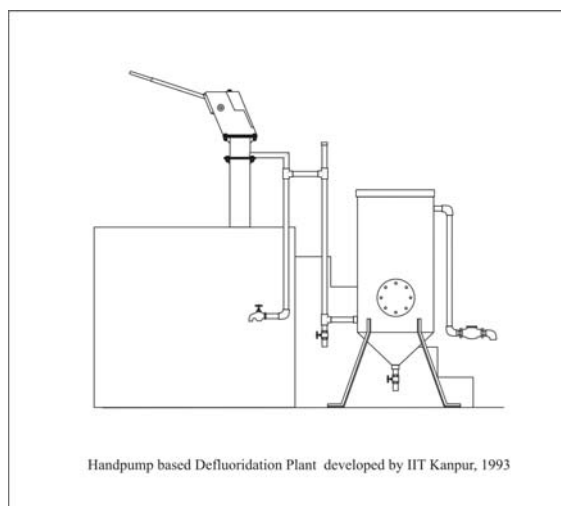
Following are the major areas of study:

1. Development of handpump attached defluoridation unit.
2. Screening of indigenous activated alumina grades in domestic defluoridation units.
3. Development of Domestic Defluoridation Units.
4. Regeneration procedure for exhausted AA and the reuse potential of AA.
5. Safe disposal of spent regenerants.

2.1. Development of handpump attached defluoridation units:

A cylindrical defluoridation unit was fabricated from MS sheet with the dimension of 0.5 m diameter and 1.5 m height. The unit was designed to operate in the upflow mode. 110 Kg of AA of grade G-87 (IPCL), having a particle size range of 0.3-0.9mm, was taken in the unit. This gave a bed depth around 55 cm. This unit was field tested at Makkur village, Unnao district U.P. For experimental study, a shallow India Mark II hand pump (≈ 35 ft depth) was installed. The defluoridation unit installation was in 1993. It required the raising of hand pump discharge level with an addition to its normal pedestal and construction of an elevated platform. Users had to go up few steps to operate the handpump. A by-pass was provided to draw the water directly from the handpump for washing and bathing.

The unit was maintained by IIT Kanpur. Raw water fluoride concentration was in the range of 6-7 mg/L. Regeneration of exhausted activated alumina was carried out *in situ* i.e. within the column. This procedure required 8-10 hrs. Average yield of the safe water (<1.5 mg/L fluoride) per cycle was around 25,000 litres. Seventeen defluoridation cycles were completed in a span of 4 years. There was no major maintenance problem during this period. There was no complaint from the users either regarding the design or the palatability of treated water. However; community help during regeneration was minimal. The unit was dismantled in 1998, as village community got an access to piped water supply. With this installation, there was no provision for spent regenerant disposal. During this period, UNICEF approach changed from community based to domestic defluoridation unit. Hence further modifications, like incorporating provision for disposal of regenerants, were not taken up.



Similar defluoridation units were fabricated and installed by M/s Gudimani for few handpumps in Shivpuri, MP. No performance details are available.

As per our knowledge, six different models (designs) of handpump attachable units (which include two different models developed by PHED Rajasthan and DST Rajasthan) have been evaluated for the defluoridation of drinking water (10 - 14). All these are either experimental units or under the supervision of PHED and / or NGOs. Out of these, one unit has been evaluated with a specific grade of Activated Alumina, AAFS - 50, manufactured by Alcal Chemicals Limited, UK. As per the manufacturers, this product has five times higher uptake capacity as compared to "normal" Activated Alumina (15). This would make it cost effective for one time use and disposal in a landfill, instead of "regeneration and reuse" required for "normal" Activated Alumina systems. Most of the field studies, with this grade, are for arsenic removal either in handpump installations or the domestic unit. PHED, West Bengal seems to have installed many handpump units (15). Trials on Fluoride removal have been

conducted on PHED handpump sites near Bhopal at various locations. Evaluation of their performance has been carried out by Regional Research Laboratory, Bhopal (14).

Comparison of performances of these handpump defluoridation unit as well as their limitations can lead to a better design. Another aspect to be considered, with handpump units, is the mode of regeneration of Activated Alumina. If *in situ* regeneration is to be carried out, then there should be a provision for the proper disposal of spent regenerants in the vicinity. A second option can be to collect exhausted activated alumina from the unit and regenerate at a central location

2.2. Screening of different grades of AA:

The search for solutions for domestic defluoridation and the discontinuation of the grade of AA used during 1991-96, mentioned earlier, led to the development of Domestic defluoridation Units (DDUs) and to the screening of indigenously manufactured grades of activated alumina for defluoridation application.

Two parameters were considered as important for the field application of activated alumina. One was fluoride uptake capacity (FUC) expressed as milligrams of fluoride removed per Kg of AA and the second was reuse potential of AA in multiple defluoridation cycles.

(a) Screening in DDU:

Since water alkalinity was known to decrease fluoride uptake capacity by AA, most of the screening studies were carried out with test water prepared by spiking ground water (IITK borewell water) with NaF. Test water fluoride concentration was generally maintained at 10 ± 0.5 mg/L. All screening tests were performed with 3 Kg AA in a IITK fabricated domestic units, (details given in a separated section). During 1991-2005, more than 15 grades of indigenously manufactured AA have been screened. Many of them are tested upto 10 defluoridation cycles, i.e. regenerating exhausted AA and reusing the same AA for the next cycle.

Under these experimental conditions used, FUC of indigenous AA grades ranged from 1500 mg/Kg AA and 2200 mg/Kg AA. Studies have also been carried out on the effect of raw water characteristics as well as AA particle size, empty bed contact time on FUC, with selected grades of AA

Presently AA grade AAFS-50 (Alcal Chemicals Co. U.K.) is being evaluated in our laboratory for fluoride uptake capacity. As mentioned earlier, this grade is reported to exhibit high FUC as compared to ordinary AA thus making it cost effective for one time use.

The main outcomes from these studies are the improvement of indigenous AA grades and their availability of in the desired particle size range.

b) General Screening procedure

A uniform testing procedure for the screening AA grades is needed, if the results from different laboratories are to be compared. Further manufactures need to test their own products for improving AA quality. UNICEF specification also required that AA manufacturer / suppliers quote fluoride uptake capacity (FUC) of their product.

Determining FUC, using fluoride spiked distilled water as test water, has no significance as other ions present in groundwater that would affect the binding of fluoride to AA, would be absent. Groundwater quality varies from place to place. Hence, a simulated groundwater, prepared by adding required chemical components, has to be used for a uniform screening procedure by different manufactures

With this view, a screening procedure was developed in our laboratory. Simulated test water was prepared by adding known quantities of NaHCO_3 , Na_2SO_4 , CaCl_2 , Na_2SiO_4 , MgCl_2 and NaF to distilled water and adjusting the pH to 7.8 ± 0.2 . Screening was performed in a PVC/Perspex column with 500 gm of AA. Details of experimental setup and procedure are given in Annual report, Jan-Dec 2004 (contract no.SSA/INDQ/2004/00000934-0).

This procedure can be used by

- (a) by manufacturers for FUC determination of their products.
- (b) For comparing different AA grades in any laboratory.
- (c) For comparing FUC of the same AA grade in two different laboratories i.e. for inter-laboratory comparison of results.

Such an approach of using simulated groundwater, for comparing different AA grades (including AAFS-50) for arsenic removal, has been recently reported by Clifford et.al. (16)

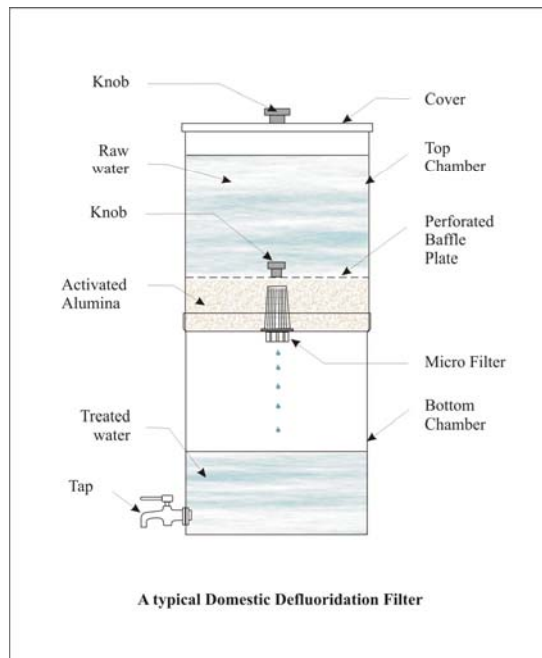
Presently column screening procedure involves intermittent flow of raw water, which simulates feed conditions. Time required for screening can be further decreased by continuously passing raw water through the column. FUC under these conditions may be less as compared to intermittent addition. However this procedure can be used for quick comparison of different grades.

2.3. Development of Domestic Defluoridation Units - DDU:

DDUs were initially designed on the assumption that 20 litres of treated water was the daily requirement for cooking and drinking for a family. With this criterion, it was expected that 3 Kg. activated alumina would be exhausted in 2 to 3 months if fluoride concentration in water was around 4 mg/L.

DDU fabricated in the laboratory consisted of two chambers, fabricated from GI sheet. 3 Kg of AA was taken in the upper chamber (24 cm dia. x 27 cm height), which gave a bed depth of 9 cm. A flow control device was fixed at the bottom of the upper chamber so as to have a flow rate of 8-10 liters per hour.

From this starting point, different versions of DDU have emerged. The quantity of activated alumina has generally become 4 Kg to 5 Kg and materials used for filter unit



include SS, HDPE (Sintex), PVC, and Terracota pots. Size of these containers is decided based on the volume of water.

FUC depends on various factors such as raw water fluoride concentration, alkalinity, pH, as well as AA grade, particle size, contact time of raw water with the sorbent and AA depth. Raw water characteristic change from location to location. AA grade, particle size (0.4-1.0 mm) and flow rate (8-10L/hr) had already been specified by UNICEF for DDU. Hence studies were carried out on the effect of AA amount and depth on specific safe water yield (SSY). SSY is defined as liters of safe water yield per kg AA

Result of these studies showed:

3 kg AA:	SSY :	117L-183L
	AA depth:	5cm-9cm
4 kg AA:	SSY :	94L-206L
	AA depth:	6.5cm-11.5cm
5 kg AA:	SSY :	133L-210L
	AA depth:	8.5cm-13.5cm

(Experimental details in Annual Report, Jan. 2004-Dec, 2004, contract no. SSA/INDQ/2004/934-0)

These observations clearly indicate the importance of AA depth in safe water yield. At least minimum of 9cm depth is to be maintained in DDU although higher depth is preferable.

Presently prototype domestic defluoridation units sent by UNICEF are being evaluated for their performance. These units have different AA grades, vary in AA amount as well as AA depth.

2.4. Regeneration of Exhausted Activated Alumina:

Regeneration of exhausted AA and its reuse for multiple cycles is one of the main advantages of using AA for defluoridation. Extensive studies were carried out on this aspect. Different regenerants used included alum, HCl, H₂SO₄ and NaOH. The results clearly indicated that efficient regeneration could be achieved with a combination of 1% NaOH and 0.4N H₂SO₄. Some screened AA grades showed less than 20% loss during 10 defluoridation cycles.

A simple 'dip regeneration procedure', appropriate for a rural set up, was developed. This required the transfer of activated alumina from domestic units to a nylon bag, dipping the bag in 10L 1 % NaOH for 8 hours (or overnight) with intermittent mixing. After washing once with raw water to remove excess alkali, the bag with AA was dipped in 10L of 0.4N H₂SO₄ for 8 hrs. This was followed by washing with raw water to raise the pH to 6. The regenerated activated alumina was ready for the next cycle.

The Dip regeneration method has been adapted in many pilot project areas in Rajasthan, A.P and UP. Main limitation of this method appeared to be intermittent mixing and the long time required for regeneration.

Presently 'Bucket regeneration' procedure' has been developed which addresses the two disadvantages of the Dip method. A plastic bucket with flow control device is used to continuously pass the regenerant over the exhausted activated alumina bed. Studies indicated

the time required for regeneration decreases substantially and changes by changing the flow rate of the regenerants. This method is more user friendly and can be easily adapted in rural setups.

Initially the regeneration procedure was optimized for 3 Kg activated alumina in the domestic unit. However, since 4 Kg to 5 Kg of AA is commonly being used, studies are being conducted to arrive at the optimal weight of AA (keeping depth of the AA bed constant) and the corresponding optimal regeneration procedure. Results have indicated that the efficiency of reuse steeply decreases with 5 Kg AA, if only 10 L of 1 % NaOH is used for regeneration.

2.5. Disposal of Spent Regenerants:

Regeneration of activated alumina generates spent alkali and acid having extreme pH values. Spent alkali regenerant would also have high fluoride concentration. Safe disposal of these regenerants is thus essential.

Different methods were tried for spent regenerant disposal. They included:

1. The addition of CaCl_2 to spent alkali regenerant to precipitate fluoride and then mix the supernatant with acid regenerant.
2. Simple mixing of spent alkali/acid regenerants.
3. Mixing alkali /acid regenerants and using certain additives like alum or lime to remove fluoride as well as to improve settling properties of the sludge.

Results indicated that overall fluoride removal of more than 85% could be achieved using option 3. Based on these findings, it was recommended that the disposal of spent regenerants can be carried out by mixing spent alkali and acid regenerants, checking pH, adding enough lime to adjust the pH 6.5-7.5 and settling the sludge for 24 hr. The supernatant solution, with low fluoride and near neutral pH, could then be drained off. It is to be however mentioned that the drain water will have high TDS, hardness and sulphate. Sludge could to be collected periodically, and used for brick making at the village level itself.

This procedure has been adopted in UNICEF assisted pilot project villages in AP and Rajasthan, for the disposal of spent regenerants.

3. HANDPUMP AND DOMESTIC DEFLUORIDATION UNITS FOR RURAL AREAS, PROS AND CONS:

Extensive literature is available on the application of Activated Alumina technology for defluoridation of drinking water in large treatment units (17,18). As mentioned earlier, this approach may not be feasible in developing countries, especially in rural areas and defluoridation solutions are needed only at the handpump or domestic levels.

Advantages of this approach are:

1. Lower cost for treatment, as only the volume of water required for cooking and drinking, which is less than 20% of total requirement, can be treated.
2. Any chemical treatment is bound to generate waste, which needs safe disposal. As lesser volume is treated, lower will be the sludge/waste production.

However success of these approaches depend upon the treatment reliability and motivation of consumers to use only the treated water for cooking and drinking, (as the untreated water is also available) as well as on various other factors.

Presently all handpump defluoridation installations, based on AA technology, are either experimental units or under the supervision of PHED. Past experience with other community units, such as iron removal, defluoridation using the Nalgonda technology, have not been generally encouraging. This is mainly due to lack of ownership by user communities and the consequent reluctance to take over management responsibility, leading to a lack of maintenance at local level by users. Other related issues are funding for maintenance, community involvement and awareness in creation of the defluoridation facility and the degree of institutional willingness to relinquish control over the installation. Under the circumstances, the sustainability of these systems under community management does not appear very encouraging.

There are six different designs for handpump attachable defluoridation units. Comparison of performance of these different units as well as their limitations may lead to a better defluoridation unit design.

Activated alumina in a handpump unit has to be periodically regenerated depending upon raw water characteristics, its fluoride concentration and amount of AA taken in the unit. There are two alternatives for the regeneration of activated alumina. One is "in situ" regeneration and the other option is by removing AA from the unit and transporting it to a regeneration centre. Regeneration of activated alumina leads to 6 to 8 bed volumes of wastewater. If the first option is chosen there should be a facility near the handpump for collecting the wastewater and its proper disposal. Hence the second option of centralized regeneration may be attractive, only if many handpump units are in close proximity. However, such a facility would have to be institutionally operated.

Convenience of access plays a major part in water source preference of users, even disregarding considerations of source potability. Handpump units may not be popular, where aquifer level is not deep (as in Makkur, UP). In such places users would be having shallow hand pumps within their homesteads and they would not prefer to get the treated water from the community hand pump.

Domestic units are the "point of use" units with a higher degree of individual ownership as DDU's have to wholly or partly paid for. This might ensure better maintenance of these units if adequate regeneration facilities are simultaneously set up at the village level. However, as in the case of handpump based units, sustenance of the technology depends on the effective back-up facility for regeneration. Awareness creation is still necessary for users to be convinced of the importance of periodical regeneration. Since regeneration will be carried out at a central place, wastewater handling and disposal can be better managed.

Regeneration is a very critical factor in AA based defluoridation, However, this position may change radically if it were possible to identify a grade of AA with a very high yield of treated water (as claimed by Alcal) so as to make it cost-effective enough to make regeneration unnecessary

References:

1. Chakraborty, D, et al. "Arsenic Calamity in the India Subcontinent what lesson have been learned", **Talanta**, **58**,3 (2002).
2. Susheela, AK "Fluorosis Management Programme in India", **Current Science**, **77**, 1250, (1999).
3. Killedar, DJ and Bhargava, DS "An overview of defluoridation methods (Part 1)", **J. IPHE**, **2**, 6 (1988).
4. Clifford DA "Ion exchange and inorganic adsorption in water quality and treatment", **Water Quality and Treatment** ,4th edition, ed. Pontius, FW, McGraw- Hill Publication, 522,(1990).
5. Rubble, F Wooseley and Dale, RD, "The Removal of excess fluoride from drinking water by Activated Alumina", **J. AWWA**,**71**,45 (1979).
6. Sharma M.R., **M. Tech thesis** submitted to the Department of Civil Engg., IIT Kanpur (1997).
7. Bulusu, KR and Nawalakhe, WG, " Defluoridation of water with Activated alumina in continuous contacting system", **Indian J. Environ. Health**, **32**, 197, (1990).
8. Rao, VK and Mahajan, Cl, "Defluoridation of drinking water in developing countries Alternative and innovative technologies", **Proc. 20th Mid Atlantic Industrial Waste conference**, p **55**, (1988).
9. Karthikeyan, G ; Menasha, S, and Apparel, BV, "Defluoridation technology based on activated alumina", **20thWEDC conference**, Colombo, Sri Lanka, 167, (1994).
10. Mishra, K.K. "Development and performance of Handpump attachable units for defluoridation of water. M. Tech thesis. Submitted to Dept. Civil Engg. IIT Kanpur (1995)
11. Venkateswara Rao, K. "Defluoridation of drinking water by Prasanthi technique" **Proc. National Workshop on defluoridation technologies for Fluorosis control** organized by Sri Krishnadevaraya University, Anantapur, p. 28 (1997)
12. Dhindsa, S.S. and Davenda, H.S. "A cost effective and simple handpump attachable defluoridation unit". **Proc. National Workshop on Control and Mitigation of excess Fluoride in drinking water**. Jaipur (India) 5 - 7th Feb. T2 - 8 (2004)
13. Kartikeyan, G. and Shunmuga Sundarraj, A. "Development of a handpump attachable defluoridation model based on Activated Alumina Technology" **Proc. National Workshop on Control and Mitigation of excess Fluoride in drinking water**. Jaipur (India) 5 - 7th Feb. T - 2(56) (2004)
14. MAGC Technologies-www.wateraid.org.uk/research/(web information)
15. Alcal Chemicals-Current News(web information)
16. Clifford, D. Arsenic Treatment Technology Demonstration, Demonstration Summary, Montana University Sys tem Water Center, Montana State University Montana,(www.water.montana.edu.) March 2001.
17. Ruble, F, "Design Manual and removal of fluoride from drinking water supplied by activated alumina", **EPA-600/2-84/134** (1984).
18. Frankel, I and Jorgen's, E "Removal of fluoride from industrial waste waters using activated alumina" , **EPA-600/2-80-58** (1980).