FLUORIDES IN WATER, DEFLUORIDATION METHODS AND THEIR LIMITATIONS

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K.R. Bulusu, B.N. Pathak, W.G. Nawlakhe, D.N. Kulkarni & V.P. Thergaonkar.

NATIONAL ENVIRONMENTAL ENGINEERING RESEARCH INSTITUTE
NEHRU MARG., NAGPUR-440020.

FLUORINE, the most electro-negative of all elements, has not only notable chemical qualities but also physiological properties of great interest and importance for human health and well-being. The chemical activity of the fluoride ion makes it physiologically more active than any other elemental ion. With low concentrations of the fluoride ion, enzymatic processes may be either inhibited or stimulated, and interactions with other organic or inorganic body components may occur that are of great importance for human physiology.

Fluorine and its properties

Fluorine is a greenish diatomic gas, F_2. Its atomic number is 9 with an electronic configuration 2, 7 ($1s^2$, $2s^2p^5$) and atomic weight 19. The great reactivity of the element is in part attributable to the weakness of the F-F bond in the fluorine molecule. Its ionisation potential, 401 KCal/g-atom, combined with dissocation energy, leads to the standard heat of formation of gaseous F^+ ion of 420 KCal/g atom (cf. Cl^+, 327; B_r^+ 301; I^+ 268). Thus even solvated cationic species are unlikely, and no evidence whatever exists for a positive oxidation state of fluorine.

The fluorine compounds are essentially of two main types, ionic and covalent, in all of which fluorine has a complete octet. Ionic fluorides contain the F^- ion. The relatively small radius of F^-, 1.36 Å, is almost identical with that of the oxide, $O^=$ ion (1.40 Å); consequently, many fluorides and

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[illegible] have very considerable [illegible] character. [illegible] shows the lowest affinity towards oxygen, which is not surprising in the light of their electro-negativities. The co-ordination number of fluorine seldom exceeds one. An important feature in the formation of fluorides is that in reactions with fluorine, the lemants usually give the highest known or maximum oxidation state. Fluorine has a strong tendency to undergo reduction from zero oxidation state to an oxidation state of minus one.

Occurrence of fluorine

Fluorine is so highly reactive that it is never encountered in its elemental gaseous state except in some industrial processes, but only in the combined form. It is the seventeenth most abundant element in the earth's crust. It is more abundant than chlorine (550 ppm) in the earth's crust. It occurs notably as fluorspar, CaF_2; cryolite, Na_3AlF_6; fluorapatite $3Ca_3(PO_4)_2\ Ca(F, Cl)_2$.

It is present as fluorspar in sedimentary rocks (lime stone, sand stone) and as cryolite in igneous rocks (granite). These fluoride minerals are nearly insoluble in water, so fluorides will be present in ground waters only when conditions favour their solution. It is also present in sea water (0.8-1.4 ppm), in mica, and in many drinking water supplies.

Micas have the general formula $W(X, Y)_{2-3}Z_4O_{10}(OH, F)_2$ where W = Na or K, X and Y = Al, Fe, Li or Mg and Z = Si or Al. The fluoride content in mica varies considerably as follows.

biotites = 970-3500 ppm ;
phlogphite= 3300-37000 ppm;
lepidolite = 19000-68000 ppm; and
muscovite = 170-14800 ppm.

Solubility data

The following are the solubilities of fluorine compounds and hydroxy apatite which are quoted in moles per litre (1).

Calcium fluoride	..	2.0×10^{-4}
Magnesium fluoride	..	1.2×10^{-3}
Fluorapatite	..	1.0×10^{-5}
Hydroxyapatite	..	6.6×10^{-5}

The solubility products for hydroxyapatite and fluorapatite are estimated by Morene (1) as follows.

Hydroxyapatite	..	$3Ca_3(PO_4)_2.Ca(OH)_2$	4.85×10^{-113}
Fluorapatite	..	$3Ca_3(PO_4)_2.CaF_2$	1.44×10^{-119}

Metabolism

The role of fluoride in animal or human metabolism is not known with any certainity. From all the work available, it is clear that a certain quantity of fluorine is essential for the formation of caries-resistant dental enamel and for the normal process of mineralisation in hard tissues. The element is metabolised from both electrovalent and covalent compounds. Low fluoride concentration stabilises the skeletal system by increasing the size of the apatite crystals and reduce their solubility. The great affinity of fluorine for calcium phosphate is perhaps the most important from the physiological point of view, that results in its accumulation in all tissues exhibiting physiological or pathological calcification. About 95 % of the fluoride in the body is deposited in hard tissues and it continues to be deposited in calcified structures even after other bone constituents (Ca, P, Mg, CO_3 and citrate) have reached a steady state. Age is also an important factor in the extent to which fluorine is incorporated into the skeleton. A similar pattern to that in bone is followed in the fluoride concentration in teeth. The uptake almost ceases in dental enamel after the age of about 30 years. From the work that has been reported (1), it is clear that physiology of human skeleton is not adversely affected by fluorides, at [illegible] upto a level of [illegible]g/1 in [illegible] water

Excretion of fluorides

The excretion of fluorides from the body is of great significance as prolonged exposure to excessive quantities is harmful. Fluorides are excreted through faeces, sweat, urine and other body fluids. Depending upon the diet, the faecal excretion accounts for 10-30 % of the daily intake. Sweating may account for as much as 50 % of the total fluorides excreted in hot climates (1). Urine usually accounts for the principal excretion of fluorides. Fluorides appear rapidly in urine after ingestion and generally the level reflects the daily intake. The loss through other body fluids is small.

Effect of fluoride ingestion in human beings and cattle

Smith & Hedge (2) have related the concentrations of fluorides to the biological effects in the tabulation below :

Concentration of fluoride, ppm*	Medium	Effect
0.002	air	injury to vegetation
1	water	dental caries reduction
2 or more	water	mottled enamel
8	water	10 % osteosclerosis
50	food and water	thyroid changes
100	food and water	growth retardation
120	food and water	kidney changes

*In water medium, ppm can be taken as equivalent to mg/l.

[illegible] certain ligaments rendering movement of joints difficult (3) is usually associated with at least 10 mg/l of fluoride in drimking water. The bone structure was found to be blurred and became diffuse structureless shadow with uneven contours. These changes were marked in spine and ribs. The acute lethal dose for man is between 2.5 and 5 g depending upon the solubility of the compound and the susceptibility of the of the man (2).

Effect of dental enamel

A condition, now known as dental fluorosis or mottled enamel, was described by Eager in 1901 among the emigrants from Italy. The term mottled enamel was first introduced by Black in 1916 in an article jointly published with McKay, in which the disease was described in details (4). The permanent teeth are particularly affected, though it occasionally affects primary teeth. It was in 1931 that a direct relationship between mottled enamel and fluoride content of water was established (5,6, 7).

In India, a disease similar to mottled enamel was first reported by Viswanathan (8) to be prevalent in human beings in Madras Presidency in 1933. In the following year Mahajan (9) reported a similar disease in cattle in certain parts of old Hyderabad State. But Shortt (10) was the first to identify the disease as ' fluorosis '. Subsequent to these findings, cases of fluorosis were reported from several other parts of the country.

Dental fluorosis occurs in human beings consuming water containing 1.5 mg/l or more of fluorides particularly during the first eight years of the life. Mottled enamel usually takes the shape of modification of tooth enamel to produce yellow or brown stains or an un-natural opaque chalky white appearance with occasional straitions and pitting. The incidence and severity of mottling was found to increase with increasing concentration of fluoride in drinking water.

... to severe. The basis for each classification of mottling was as follows (quoted from Ref. No.1, p.230).

1.	Normal	:	The enamel is translucent, smooth and presents a glossy appearance.
2.	Questionable	:	Seen in areas of relatively high endemicity. Occasional cases are border line and one would hesitate to classify them as apparently normal or very mild.
3.	Very mild	:	Small, opaque, paper-white areas are seen scattered irregularly over the labial and buccal tooth surfaces.
4.	Mild	:	The white opaque areas involve at least half of the tooth surface, and faint brown stains are sometimes apparent.
5.	Moderate	:	Generally all tooth surfaces are involved, and minute pitting is often present on the labial and buccal surfaces. Brown stains are frequently a disfiguring complication.
6.	Moderately severe	:	Pitting is marked, more frequent and generally observed on all tooth surfaces. Brown stains, if present, are generally of greater intensity.
7.	Severe	:	The severe hypoplasis affect the form of the tooth. Stains are widespread and vary in intensity from deep brown to black. This condition may sometimes be referred to as ' corrosion' type of mottled enamel.

Dean, et. al (13) derived a mottled enamel index of the community, which was defined in terms of the degree of severity of mottled enamel observed clinically. There is possibly no such data available in India to evaluate Communi... ...ex of Fluorosis or Fluorosis Index, in the abs... ...which, the permissive or excessive limits to f... ...n drinking water are only arbitrary.

C, ppm [illegible] 0.34/E

$E = (-0.038+0.0062\ t)$ = estimated daily average water consumption for children of ten years of age, in terms of ounces of water per pound of body weight.

where t = annual mean of daily maximum temperature (^{o}F).

The Ministry of Health, Government of India had prescribed 1.0 and 2.0 mg/l as permissive and excessive limits for fluorides in drinking water.

Incidence of fluorides in river waters in India

The fluoride content of few rivers, streams and springs are presented in Table 1 (15).

Incidence of fluoride in groundwater

Occurrence of fluoride bearing waters was reported by many workers from time to time in Andhra Pradesh (16), Rajasthan (17), Punjab & Haryana (18), Maharashtra (19), Tamil Nadu (15), Karnataka (20), Madhya Pradesh (21), Gujarat (22) and Uttar Pradesh (23).

Raghava Rao (24) reviewed the results of surveys conducted in the country to identify the areas of fluoride incidence in groundwater and the following information is from his review. The areas in the individual states have been categorised by him into four groups showing the concentration in the range 0-1.5, 1.5-4.0, 4-8 and over 8 mg/l in Arid and Semi-arid belts and Western Central India in the Southern States, the groups are arranged in the ranges 0-1.5, 1.5-5 and more than 5 mg/l (Tables 2 to 5).

		,,	[illegible]
[illegible]	[illegible]	,,	0.35
[illegible]*	[illegible]sagar, Raja[illegible]than	Alluvium & Aeolean sand	4.0
Narmada	Jamtara, Jabalpur, M.P.	Alluvium	0.1
Netravati	Mangalore, Karnataka.	Alluvium costal	0.1
Periyar	Alwaye, Kerala	,,	0.1
Chalakudiyar	Chalakudiyar, Kerala.	,,	0.1
Mahanadhi	Rajim, M.P.	Vindhyan , Limestone & shales	0.1
Indravati	Chitrakut, M.P.	,,	0.4
Vekkilu	Chagla Marri, A.P.	,,	1.5
Krishna	Vijayawada	Khondalites	1.0
Krishna	Nagarjun Sagar, A.P.	Cuddapah Quartzites	1.0
Paleru	Rajapet, A.P.	Archaean Granite	1.5
Sabri	Chitoor, A.P.	,,	1.0
Indravati	Bhopal Patnam	,,	1.0
Gundala (Hotspring)	Godavari Bed, Gundala, A.P.	,,	3.0
Muneru	Khammam, A.P.	,,	2.0
Bhima	Yadgir, Karnataka	,,	1.5
Chitravati	Dharmavaram, A.P.	,,	3.5
Pennar	Pamidi, A.P.	,,	1.5
Tambraparni	Tirunelveli, Tamil Nadu	,,	3.5
Vaigai	Madurai, Tamil Nadu	,,	1.0
Amravati	Darapuram, Tamil Nadu	,,	1.0
Kongal	Nalgonda, A.P.	,,	2.0
,,	Yellareddiguda, Nalgonda, A.P.	,,	12.0
Machna* Watershed	Betul, M.P.	,,	6.0
Chandora* Watershed	Multai, M.P.	Deccan Trap	5.3

*Ground water sample.

[illegible]	[illegible]	[illegible]
(b) [illegible]	(b) [illegible]	[illegible]
(c) Anjeri	(c) Bijasan	
(d) Waghta-choti	(d) [illegible]	

TABLE 3

FLUORIDE CONCENTRATION - SOUTHERN STATES OF INDIA (24)

State	Range of fluoride in ground water in ppm: 0.0-1.5	1.5-5.0	More than 5
Andhra Pradesh	(a) Anantapur Dist. (b) Chitoor Dist. (c) Medak Dist.	(a) Anantapur Dist. (b) Hyderabad Dist. (c) Krishna Dist. (d) Kurnool Dist. (e) Nalgonda Dist. (f) Prakasam Dist.	(a) Anantapur [illegible] (b) [illegible] (c) [illegible]
Tamil Nadu	..	(a) Coimbatore Dist. (b) Dharmapuri Dist. (c) Madurai Dist. (d) North Arcot Dist. (e) Salem Dist. (f) Tiruchirapalli Dist.	

Contd.. TABLE 4

State	Range of fluoride in Ground-waters, ppm			
	0.0-1.5	1.5-4.0	4.0-8.0	More than 8
Rajasthan		(f) Eastern and Western parts of Nagaur Dist	(f) Western part of Nagaur Dist.	
		(g) South-Eastern part of Alwar Dist.		
		(h) Southern & Northern parts of Bharatpur Dist.		
		(i) Southern part of Jaipur Dist.		
		(j) North Western part of Barmar Dist.		
		(k) Northern part of Tonk Dist.		
		(l) Eastern and Southern part of Jalore Dist.		
		(m) Northern part of Sirohi Dist.		
Gujarat		(a) Part of Banaskantha Dist.	(a) South Eastern and Western parts of Mehasana Dist.	(a) Naliya in Kutch Dist.
		(b) Part of Mehasana Dist.	(b) Southern part of Kutch Dist.	
		(c) Part of Kutch Dist.	(c) Western part of Jamnagar Dist.	
		(d) Part of Surendra Nagar Dist.		
		(e) Parts of Ahmedabad		

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TABLE 5

FLUORIDE CONCENTRATION - ARID & SEMI-ARID BELTS OF WESTERN INDIA

State	Selective location of high fluoride concentration		
	Village.	Geological horizon	Fluoride concentration (ppm)
	(a) Gulabpura	Biotite Schist	9.5
	(b) Phagi	-	3.5
	(c) Chirawa	Quarternary alluvium	8.5
	(d) Sagalia	-do-	19.0

The general level of fluorides in groundwaters is usually between 1 and 5 mg/l except in a few cases, where the concentrations are reported as high as 19 mg/l.

Removal of fluorides from water

Several methods have been suggested from time to time for removing excessive fluorides. These may be divided into two basic types - those based upon an exchange process or adsorption; and those based upon the addition of chemicals to water during treatment. The materials reported to have been used in the contact beds include processed bone, natural or synthetic tricalcium phosphate, hydroxy-apatite, magnesia, activated alumina, activated carbons and ion exchangers. Chemical treatment methods include the use of lime either alone or with magnesium salts and aluminium salts either alone or in combination with a coagulant aid. Other methods include the addition to fluoride water of materials like magnesia, calcium phosphate, bentonite, fuller's earth, bentonite and diatomaceous earth, mixing and their separation from water by settling and or filtration. All these methods suffer from one or the other draw-backs; high initial cost, lack of selectivity for fluorides, poor fluoride removal capacity, separation problem, complicated or expensive regeneration. Some of these materials are dealt here briefly.

Phosphatic compounds

These include several bone formulations, synthetic tricalcium phosphate and a mixture of calcium phosphate and hydroxy-apatite (25, 26, 27 & 28).

Processed bone : The bone is degreased, dried and pulverised to 40-60 mesh size. The powder is carbonised in a closed retort at 1380-1740°F. The product contains tricalcium phosphate and has a capacity to remove 1000-1500 mg F per litre of medium. After saturation with fluorides, it can be recalcined at around 750°F, under restricted air supply to restore the adsorbing capacity of the char. Alternatively, the bed may be regenerated by sodium hydroxide solution.

Bone charcoal : The bone is processed by burning in air and pulverising to -60, +100 mesh. The fluoride removal capacity of the product is 1000 mg F per litre of media.

Synthetic tri-calcium phosphate : The product is prepared by reacting phosphoric acid with lime. It has a capacity of 700 mg F per litre. The medium is regenerated with 1 % sodium hydroxide solution, followed by a mild acid rinse.

Florex : It is a trade name for a mixture of tricalcium phosphate and hydroxy-apatite. The fluoride removal capacity of the medium is 600 mg F per litre and is regenerated with 1.5 per cent sodium hydroxide solution. Florex was tried in Pilot Plant at Climax, Colo, U.S.A. in 1937 and Scobba, Miss, U.S.A. in 1940 but without much success owing to high attritional losses and the plants were abandoned (29, 30).

Activated alumina : The use of this material for the removal of fluoride ion from drinking water appears to have been first suggested by Boruff in 1934 (25). The bed was regenerated with a 2 % solution of sodium hydroxide, followed by neutralisation of the excess alkali with dilute hydrochloride acid. The capacity of the medium was found to be about 800 mg F per litre of alumina. Many modifications of the process were suggested by subsequent workers. Several patents based on the use of aluminium oxide for fluoride removal were issued to Heinzel and Churchil in 1936, Goetz in 1938, and Urbain and Stemen in 1940. Savinelli and Black (31) have used filter alum to regenerate activated alumina bed. The capacity of aluminium to remove fluorides was reported to be proportional to the amount of filter alum used for regeneration upto a level of about 0.2 kg alum per litre (12 lbs alum per cft) of alumina. At this level, the fluoride removal capacity was approximately 5,500 mg F per litre of alumina. The most important single factor affecting the fluoride exchange capacity of alumina was the alkalinity of the influent water.

Lime : It has been observed that while giving lime treatment to waters containing magnesium salts, fluorides are absorbed on magnesium hydroxide flocs and it results in fluoride removal (25, 32, 33). Empirically, the amount of fluoride removed is equal to $0.07\ F\sqrt{Mg}$, where F represents mg fluoride initially present and Mg the mg of magnesium removed in the form of flocs. In this case, the water must be treated to a caustic alkalinity of 30 mg/l, a pH of 10.5 or above and as such recarbonation is necessary (34). Magnesia and calcined magnesite have also been used for fluoride removal from water and the fluoride removal capacity was reported tobe better at high temperatures (35).

Activated carbons : Most of the carbons prepared from different carbonaceous sources showed fluoride removal capacity after alum impregnation. McKee and Johnston (36) have reported good fluoride removing capacity of various types of activated carbons. Srinivasan (37) prepared a carbon from paddy husk by digestion in 1 % KOH and soaking it over-night in 2 % alum solution. The material removed about 320 mg F per kg (150 mg F per l) and showed a maximum removal efficiency of pH 7. The carbon was regenerated by soaking the spent material in 2 % alum solution for 12-14 hours. A pilot plant with this material was installed at Guntakal, Andhra Pradesh to treat water containing 2.8 mg F/l which was since abandoned. Activated carbons prepared by other workers from cotton waste, coffee waste, cocomut waste etc. were tried for defluoridation but all these materials were of academic interest only.

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Ion exchange resins : Strong base exchange resins remove fluorides either on hydroxyl cycle or chloride cycle along with anions (38, 39). Since the proportional quantity of fluoride as compared to other anions is very small, the effective capacity of such resins works out quite low. There are no known commercial anion exchange resins which are selective for fluoride only. Some inorganic ion exchangers e.g., complex metal chloride silicate, formed from barium or ferric chloride with silicic acid, also exchange fluoride for chloride.

Cation exchange resins impregnable with alum solution have been found to act as defluoridating agents. Various workers (40, 41, 42) have used cation exchange resins after treatment with alum solution for defluoridation. Venkataraman et. al (43) reported that ' Avaram Bark ' based cation exchange resins works effectively in removing fluoride from water.

Other laboratories connected with defluoridation studies in India

Attempts were made by several workers since 1933 to develop suitable methods of defluoridation. Investigations were carried out at Indian Institute of Science, Bangalore; King's Institute, Guindy; Indian Council of Medical Research, New Delhi; Central Salt and Marine Chemicals Research, Bhavnagar and Geological Survey of India. No plant of any significant size was installed for removing fluoride by any of these laboratories.

Defluoridation work at NEERI

The work on defluoridation was taken up by NEERI in 1961 on a reference from some State Governments afflicted with the problem (19). A review of the materials developed by different workers on defluoridation revealed that most of the methods involve acids and alkali either during pretreatment or regeneration and are not suitable for Indian conditions. The phosphate compounds and ion exchange material are not practicable on large scale. Paddy husk carbon demonstrated by Srinivasan (37) has a low capacity and poor attritional quality.

Several materials like clays, minerals, ion exchange resins, activated carbons, activated alumina, sulphonated coals and serpentine were tried at NEERI for the removal of excess fluorides from water. Chemical treatment, <u>in situ</u>, with lime, magnesium salts, iron and aluminium salts were also studied. Only those that showed an encouraging trend on bench-scale and studied in details, are presented in this paper. These include ion exchange resins, saw dust carbon, coconut shell carbon, defluoron-1, carbion, magnesia, serpentine and defluoron-2. Ion exchange resins, saw dust carbon, defluoron-1, magnesia and serpentine did not prove useful beyond bench-scale.

Pilot plant studies were carried out at Gangapur, Rajasthan using carbion. Full size plants were installed using defluoron-2, at Municipal Corporation, Nalgonda and Central Training Institute, Hyderabad, Andhra Pradesh.

<u>Ion exchange resins</u>

<u>Anion exchange resins</u> : Polystyrene anion exchange resins in general and strongly basic quaternary ammonium type resins in particular are known to remove fluorides from water along with other anions (18, 19). Bhakuni (19) has studied and compared the following resins on bench-scale.

Polyanion exchange resin (HCL)
Tulsion A-27
Deacidite, FF-IP
Lewatit, MIH-59
Amberlite, IRA-400

Glass columns of 22 mm dia were filled with 60 ml resin and a flow-rate of 0.4[illegible] lpm/litre (3 gpm /cft) was used. The treated water was collected in one litre aliquots and the columns were regenerated using 0.16 kg NaCl per l (10 lbs /cft) or 0.12-0.16 kg NaOH per l (7-10 lbs per cft).

The results (p. 93 Ref. 19) recalculated by the authors are summarised in Table 6.

TABLE 6

FLUORIDE REMOVAL BY ANION EXCHANGE RESINS

Resin	Form	Calculated capacity, mg F/l	Test water fluorides, mg F/l	Cost of treatment per m^3 Rs.	Capital cost per m^3 Rs.
Tulsion A-27	Hydroxyl	32	2.8	7.95	1422
Deaceodite FF-1P	"	130	2.8	2.35	1000
Lewatit MIH-59	"	96	2.8	3.00	1043
Amberlite IRA-400	"	232	2.8	1.55	939

The table 6 indicates that the resins studied yields 20-145 bed volumes of defluoridated water per cycle. Subsequent experience showed that these resins loose their fluoride removal capacity on prolonged use (10-15 cycles) and a total replacement becomes necessary. A layer of white deposits was developed over the resin beds and this may be the reason for this drop in the capacity.

The cost of treatment was calculated on the basis of a pressure type of plant capable of holding 1,410 l of medium. The capital cost of the plant was Rs. 70,000/-. The depreciation of plant and medium was taken as 20 % and 50 % per annum respectively. The cost of treatment included the cost of chemicals, depreciation, power and operational charges and the cost of treatment per cubic meter was arrived at from the following formula.

$$\frac{2867a + 17.7C}{33.8C}$$

where C = capacity of the medium corresponding to the raw water fluoride and alkalinity concentrations; and

a = concentration of raw water fluoride.

Thus the anion exchange resins were found to be of relatively low capacity for fluoride removal. The cost of anion resins is Rs. 20/- to Rs. 35/- per litre and the results indicate that anion exchange resins are not economical to be used in removing fluorides from water. Besides, the strong base anion exchange resins impart a typical taste to the treated water which may not be acceptable to the consumers.

<u>Cation exchange resins</u> : Bhakuni (44) has compared the performance of saw dust carbon, defluoron-1, carbion, wasoresin-14 and a polystyrene cation exchange resin, using glass columns of 33 mm dia, flow rate of 270 ml per min per litre of medium (1.7 gpm /cft) and 4.3 mg F/1 test water and 50 ml aliquots of resin was used in these studies. When the residual fluoride concentration reached 1.5 mg F/1, the bed was regenerated with 200 ml of 1 % alum solution and washed with tap water.

The results of the study (44) as recalculated by the authors are summarised in Table 7. The last three columns are arrived at on the basis of a pressure type plant capable of holding 1,000 litres medium and designed flow rate of 4 M^3/hr. The regenerant is 1 % alum solution and at the rate of 40 kg filter alum for each m^3 of medium. The cost of alum was taken at Re. 0.70 per kg. The power charges were taken as Re. 0.10 per unit to pump water against a total head of 18 meters. The depreciation on plant and medium was taken as 20 % and 40 % respectively. The cost of treatment included the cost of chemicals, depreciation, power and operational charges and was arrived at by the following formula.

$$\frac{24.92C + 2834.6a}{96C}$$

Where capacity of the medium is given by 'C' as mg F/1 and the raw water fluorides concentration by 'a' (mg/1).

TABLE 7

FLUORIDE REMOVAL BY CATION EXCHANGE RESINS

Medium	Calculated capacity, mg F/l	Test water fluorides, mg F/l	Bulk density, g/l	Cost of treatment per m^3 Rs.	Capital cost per m^3 Rs.
Carbion	320	4.3	680	0.65	258
Wasoresin-14	262	4.3	730	0.74	315
Polystyrene resin	420	4.3	850	0.56	197
Sulphonated saw dust carbon	370	4.3	620	0.60	285

Ramakrishna et al (45) prepared an ion exchange material from coffee husk by treatment with sulphuric acid, sodium chloride and alum and found it efficient in removing fluorides. Subsequently Mohanrao and Pillai (46) adopted this method for preparing an active carbon from spent coffee grounds. Seethapatirao (47) had adopted the same procedure for bench scale to prepare a sulphonated carbon from coconut shell, which he found it to be satisfactory in removing fluoride from water. The regeneration was with 200 ml of 1 % alum solution. The capacity and the bulk density are calculated as 270 mg F per l and 0.62 kg/l respectively. No laboratory studies of any significance were reported.

Saw dust carbon : [illegible]ni (48,49,50) prepared a carbon from saw dust obtained from saw mills processing woods like sagon, sheesham and teak by heating the material in a closed vessel and allowing the fume to escape. The carbonised saw dust quenched in a 2 % alum solution was washed free of the excess alum. On exhaustion, the carbon was regenerated by passing two bed volumes of 0.5 % alum solution.

... /kg ... ... The carbon was studied for a total of 22 cycles of ... ation. The material had the problem of excessive att... itional losses and appreciable head loss.

The saw dust costs Rs. 5.00 to Rs. 6.00 per bag of about 100 litres capacity and to this are to be added the charges of sieving, carbonisation and alum treatment. No large scale studies have been reported using this medium because of its poor hydraulic characteristics.

Defluoron-1

Defluoron-1, a sulphonated saw-dust impregnated with 2 % alum solution was developed by Bhakuni (19,44). It was prepared by treating 20-40 mesh saw dust with sulphuric acid, washing the excess acid, soaking the sulphonated product in alum solution for two hours and finally washing it to remove the excess alum. The recovery of sulphonated product was 56.3 to 69.? per cent of dried saw dust. The bulk density of the medi... is 620 g per litre. Bhakuni studied this medium in great details in the laboratory and has carried out moderate field trials. A domestic defluoridator was also prepared with this medium for use by individuals (19).

Laboratory evaluation of the medium was carried out by using 75 ml medium, 4.5 mg F/l test water and a flow rate of 0.48 l/min/l. The pH of the test water was adjusted to 6. The total volume of water treated upto a breakthrough of about 1 mg F/l was 8 litres*. The average fl... removal capacity of 75 ml medium works out as 8 (4.5-1.0) = 28 mg F which is equivalent to 370 mg F/l or about 600 mg F/kg of medium. Field studies were made

... (p. 130) in Ref. No. (19).

TABLE 16

SETS OF LABORATORY EXPERIMENTS CARRIED OUT BY JAR TEST ON NALGONDA TECHNIQUE

Table No	Alkalinity, mg $CaCO_3$ /l	Fluoride, mg F/l
17	80	2.05-4.70
18	125	2.15-5.80
19	200	2.30-6.30
20	310	2.25-10.20
21	400	2.20-10.20
22	500	2.30-10.20
23	600	1.95-10.20
24	820	2.00-10.40
25	1070	2.10-10.50

The alum dose was varied according to experimental necessity and attempts were made as far as possible to lower fluoride below 1 mg F/l in the treated water. However, the alkalinity was found limiting in some experiments and the fluorides could not be lowered to the desired level. It indicates that adequate alkalinity is essential to achieve the fluoride level of 1 mg/l (or lower) in the treated water. The results are shown in Table 17 to 25.

Based on the laboratory and field studies, the quantity of alum required to reduce the fluorides to excessive and permissive limits are worked out in terms of mg filter alum per litre of water. The doses are shown in Table 26.

Defluoridation of higher fluoride concentration

Water with high fluoride concentration are economically treated by split treatment. For example, a raw water containing 14-15 mg F/l and alkalinity 268 mg/l $CaCO_3$ and pH 8.3 needed 2,500 mg/l alum dose in straight treatment. But when the same water was treated in two stages by giving 500 mg/l alum and 25 mg/l lime in first stage allow to settle amd take out the supernatant and add 250 mg/l lime and 500 mg/l [illegible] (2.2-1.0) = 51.2 mg F removal capacity per litre of defluoron-1 (50 mg F/kg).

Bhakuni (p. 152. ref. 19) presents the break-through capacity (upto a leakage of 1.0 mg/l) as upto 3000 mg/kg, with an optimum of 1600 mg F/kg (1000 mg F/l) under normal conditions of water treatment. However, a recalculation on the basis of his data reveals a maximum workable capacity of 370 mg F/l (600 mg F/kg) only. The medium was not be tested on any pilot plant scale, but the experience of the authors indicate that the medium has poor hydraulic properties and suffered from heavy attritional losses.

The fluoride removal cost shown in Table 7 are on the basis of laboratory studies and work out to be Re. 0.60 per m^3 of water containing 4.3 mg/l fluorides.

Carbion

Carbion is a cation exchange resin of good durability and can be used both on sodium and hydrogen cycles. It has a bulk density of 680 g/l with a grading of -16, +30 mesh.

Laboratory experiments using 50 ml aliquots (44) of 4.3 mg F/l test water and regeneration using 200 ml of 1 % alum solution indicated an average fluoride removal capacity of 320 mg F/l or 470 mg F/kg carbion. On the basis of these column studies in the laboratory, the cost of treatment worked out to be Re. 0.65 per m^3 @ Rs. 700/- per tonne of alum (Table 7).

A pilot plant was installed using a mixture of this medium with defluoron-1 in the proportion of 8 : 1 at Gangapur (Rajasthan). The plant comprises a cylindrical tank of 610 mm dia by 1830 mm height, two alum tanks and a raw water overhead tank (19). The plant was charged with 224 litres of carbion and 28 litres of defluoron-1.

Filter alum solution of 2, 3, 5, 6 and 10 % was used to regenerate the mixed medium. The corresponding amount of alum was 18, 18, 30, 30 and 30 kg (Table 63, p. 167, ref. 19). The fluoride content of the raw water was 4.8 mg F/1. In all 29 cycles of operation were studied. During the first few cycles of operation, most of the defluoron-1 was washed out during backwash operation due to its light weight and what eventually remained in the plant was essentially carbion. The results of the study were as follows.

Analysis of Gangapur Plant Data

Cycle of operation	..	29
Regenerant concentration	..	2,3,5,6 and 10 %
2 %	..	8 cycles (144 kg alum)
3 ..	..	5 .. (90 ..)
5 ..	..	4 .. (120 ..)
6 ..	..	1 .. (30 ..)
10 ..	..	10 .. (300 ..)
20 ..	..	1 .. (30 ..)
Total quantity of water treated	..	8 53.3 m^3
Total alum used in 29 cycles	..	714 kg

Fluoride in treated water (mg F/1)

Maximum	..	1.45-2.50
Minimum	..	0.16-0.90
Composite	..	0.30-1.60

On the basis of the studies at Gangapur, the average fluoride removal capacity of carbion was evaluated as 364 mg F/l of medium, working on a raw water with an alkalinity of 350-360 mg/l. On this information and using a pressure unit with m^3 carbion with 4 m^3/h flow rate, cost of treatment of water is computed using the following relationship.

$$\text{Cost per } m^3 = \frac{97.5 \times C + 146 \times a}{96 \times C}$$

where C = capacity of medium per litre, and
a = raw water fluoride mg F/l

The cost of treatment per m^3 works out to be Rs. 1.03 to treat raw water with 4.3 mg/l fluorides. The cost includes capital, depreciation, power, filter alum and personnel.

Magnesia

Investigations (51,52) to study the usefulness of magnesia in fluoride removal were conducted. Crystalline magnesium hydroxide was obtained by reacting a magnesium salt with milk of lime. The precipitate was filtered, washed and dried. The dried product was calcined at 1000°C for 3 hours to obtain magnesia. Varying quantities of magnesia were added to one litre aliquots of test water and stirred for 30 minutes using a jar test machine. Fluoride contents were estimated on one hour settled sample.

A typical groundwater containing 10 mg/l fluorides, 60 mg/l hardness, 500 mg/l alkalinity and 7.6 pH was studied using magnesia (MgO) concentrations of 10-1500 mg/l. The treated water showed a pH above 9. The average fluoride concentration in the filtrate was 5.8 mg F/l where the dose was 1000 mg/l. The fluoride at 100, 250 and 500 mg/l doses were 9.5, 8.9 and 8.4 mg F/l respectively. A dose of 1500 mg/l magnesia and a contact period of 3 hours was required to reduce the fluoride content in the water to 1 mg/l.

The study established that magnesia removed the excess fluorides, but large doses were necessary. Moreover, the pH of the treated water was beyond 10 and its correction by acidification or recarbonation is necessary. All this adds to the cost and complexity of operations. The acid requirement can be to the extent of 300 mg/l expressed in terms of $CaCO_3$/l.

The experiments using 90 ± 5 per cent magnesia thus revealed the limitations of this process under the present stage of development in the country. The high initial cost, large concentrations required, alkaline pH of the treated water and complexity of the preparation of magnesia are the inhibitive factors to render it acceptable in the field.

The cost of treatment using magnesia is calculated on the following basis for a typical plant capable of producing 2,270 M^3/d water.

Units : Magnesia slurry preparation tanks, dosing tanks, mixing tanks with three hours contact period, settling tanks of three hours, sedimentation period, pH adjustment units with sulphuric acid dosing equipment (with chlorination equipment and overhead storage tank).

(a) Capital works

Civil works	..	Rs.	4,80,000/-
Machinery, piping and equipment	..	Rs.	1,50,000/-
Land	..	Rs.	20,000/-
total	..	Rs.	6,50,000/-

(b) Depreciation

Civil works @ 3.33% per annum.	..	Rs.	16,000/-
Machinery, piping and equipment @ 6.66% per annum.	..	Rs.	10,000/-
total	..	Rs.	26,000/-

.. 25

(c) Interest on the capital

@ 10 % on the capital	..	Rs.	65,000/-

(d) Personnel .. Rs. 42,000/-

(e) Maintenance

Civil works @ 2% per annum	..	Rs.	9,600/-
Machinery etc. @ 5 % per annum	..	Rs.	7,500/-
total	..	Rs.	17,100/-

(f) Operational cost

Depreciation	..	Rs.	26,000/-
Interest on capital	..	Rs.	65,000/-
Personnel	..	Rs.	42,000/-
Maintenance	..	Rs.	17,100/-
total	..	Rs.	1,50,100/-
Say	..	Rs.	1,50,000/-
or	..	Rs.	411/- per day

(g) Running cost (chemicals)

Magnesia required for defluoridation of raw water containing 4.3 mg F/l and 215 mg/l alkalinity.	..	900 mg magnesia/litre
Sulphuric acid required to reduce the pH to 8	..	50 mg/l (appx)
Cost of magnesia	..	Rs. 1.20 per kg.
Cost of sulphuric acid	..	Rs. 1.00 ,, ,,
~~Cost~~ Magnesia consumption per day	=	2.27 x 900 = 2.043 kg
Su-lphuric acid consumption per day	=	2.27 x 50 = 113.5 kg

Total cost of chemical treatment per day

= (2043 kg x Rs. 1.20/kg + 113.5 kg x Rs. 1.00 per kg)

= Rs. (2,451.6 + 113.5) = Rs. 2,565.10

(h) Running costs (power) .. Say 300 units/day

@ Rs. 0.20 per unit, cost of power = Rs. 60/- per day.

(i) Total operational costs/day

= Rs. (411.00 + power + chemicals)

= Rs. (411.00 + 60.00 + 2,565.10) = Rs. 3,036.10

(j) Operational costs per m^3 water treated

Total cost/day ÷ quantity of water treated

= 3,036.10/2,270 = Rs. 1.34 per m^3

.. 26

Thus the operational cost works out to be Rs. 1.34 per m^3 using magnesia.

Serpentine

Serpentine as a mineral name, applies to the material containing one or both of the minerals, chrysotile and antigorite. The composition of the mineral closely corresponds to the formula $Mg_6Si_4O_{10}(OH)$. The material is green or yellow and is available in Andhra Pradesh. To test the capacity of serpentine to remove fluorides from waters, the green and yellow varities were studied for their defluoridation capacity. Extensive laboratory investigations were conducted with a view to popularize the mineral, if found suitable as defluoridating medium.

Jar tests, bottle and column experiments were conducted using different sizes of the mineral (53,54). The lumps (50-100 mm in size) are crushed, pulverized and sieved to obtain -16, +30 ; -30, + 60 ; -60, + 100 and -100 mesh fractions. The mineral is hard and is difficult to pulverize, particularly to sizes below -30 mesh. Manual crushing gave an average yield of 65-67 % by weight.

Jar tests : Jar tests were made on water with 280 mg alkalinity/l and 6.5 mg F/l. Stirring* was at 60-80 rpm for 45 minutes with amineral dose of 100-1000 mg/l (-100 mesh size). With 1000 mg/l dose, the fluorides were 6.0 mg F/l in the treated water. The material rapidly in the beakers during test. A comparative evaluation was made using green and yellow varieties of serpentine, dose upto 80 g/l, and 6.2 mg F/l test water. The results are shown in Table 8.

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*Phipps & Baird Electrical Jar Test was used.

TABLE 8

COMPARATIVE PERFORMANCE OF GREEN AND YELLOW VARIETIES OF SERPENTINE (-100 MESH POWDER) JAR TESTS (54)

	Green variety						Yellow variety					
Dose, g/1	0	10	20	40	60	80	0	10	20	40	60	80
Fluorides, mg F/1	6.2	4.8	4.2	2.6	2.5	1.9	6.2	4.6	3.7	2.7	2.2	1.8
pH	8.4	8.4	8.6	8.7	8.8	8.9	8.4	8.4	8.6	8.8	8.8	8.9

Bottle experiments : A dose of 10-250 g of mineral (green) of -100 mesh size was added to each litre of test water containing 6.5 mg F/1. The contents were agitated viroously in wide mouth bottles for 5 hours using a mechanical vibrator and allowed to settle overnight. The supernatant was filtered and tested for fluorides. About 80 g/1 mineral was found necessary to reduce the fluorides from 6.5 mg/1 to 1.0 mg/1, which is the permissible limit of Ministry of Health, Government of India for fluorides in drinking water.

Column studies : Studies were conducted using columns of 50 mm dia charged with 1.5 litres of -16, +30; or -30, +60 mesh size serpentine. A flow rate of 1.5 l/h (15.7 gph/sq.ft) was used to commence with, which dropped steadily with the progress of the run. The results are shown in Table 9.

The cost of treatment is worked out on the basis of a pressure unit capable of holding 1.41 m^3 yellow variety serpentine of -16, +30 mesh size and one meter depth for a flow rate of 1 m^3/1 water with 6.0 ± 0.2 mg/1 fluoride at 340 ± 40 mg/1 alkalinity. Water obtainable from this unit is about 34 bed volumes or 48 m^3. The serpentine is not regeneratable and requires to be filled each time after treating this volume of water.

TABLE 9

DEFLUORIDATION CAPACITY OF YELLOW AND GREEN VARIETIES OF SERPENTINE (48)

	Yellow Variety				
Fraction	-16, + 30 mesh			-30, + 60 mesh	
Test water fluorides, mg F/l	3.0	6.1	10.4	2.9	10.5
Test water alkalinity, mg $CaCO_3$/l	250 ± 30	350 ± 30	900 ± 20	280 ± 30	950 ± 20
Quantity of water obtained, l	70	48	12	65	20
	Green variety				
Fraction	-16, + 30 mesh			-30, + 60 mesh	
Test water fluorides, mg F/l	2.8	5.8	10.5	2.5	10.5
Test water alkalinity, mg $CaCO_3$/l	280 ± 30	300 ± 10	1000 ± 30	350 ± 20	1000 ± 30
Quantity of water obtained, l	21	14	2	44	8

To obtain 1.41 m^3, serpentine, quantity of mineral required to be handled will be on the following basis.

Weight of 1.41 M^3 serpentine	..	1.410 x 1000 x 2.5
	=	3,525 kg.
Maximum recovery on processing	..	70 %
Quantity of serpentine to be processed	..	3,525 ÷ 0.70
	=	5,000 kg.

Processing costs of Serpentine

Cost per tonne	..	Rs.	50.00
CST @ ,, ,,	..	Rs.	15.00
Freight ,,	..	Rs.	15.00
Paking & forwarding	..	Rs.	10.00
Crushing, pulverising & sieving per ton.	..	Rs.	30.00
Total cost per tonne	..	Rs.	120.00

[illegible] tonnes = Rs. [illegible]

Cost of plant	..	Rs.	15,000/-
Depreciation @ 10 %	..	Rs.	1,500/-
	or	Rs.	4.10 per day

One charge of 1.41 m^3 serpentine treats 48 m^3 @ 1 m^3/hr.
Assuming only 8 hour operation/day, one charge lasts for 6 days only.

i.e., depreciation on serpentine	=	Rs.	600/-
	=	Rs.	100/- per day

Ignoring pumping costs and also operator charges, cost of treatment per day works out to be Rs. 104.10 per day for treating 8 m^3 water.

Cost of treatment = Rs. 104.10 ÷ 8 = Rs. 13/- per m^3

It is concluded that cost of defluoridation is prohibitive with serpentine.

Defluoron-2

To overcome the problems faced with saw dust carbon and defluoron-1, a medium ' defluoron-2 ' was developed in 1968 for the removal of fluorides from drinking water (55,56). Extensive trials with the medium, both on the laboratory and in the field have shown that, it does not suffer from most of the handicaps like some of the indigenous materials developed earlier.

Defluoron-2 is a sulphonated coal and works on the aluminium cycles. It was found to give the best results with one bed volume of 4 % (w/v) alum solution as regenerant. A bed volume is equal to the volume of media in the unit. The life of the medium was found to be 2-4 years.

Laboratory studies

To study the effect of prolonged use of this medium on fluoride removal capacity, work was carried out to an aggregate of 55 cycles of continuous operation of 100 mm diameter column charged with a total of 6 litres of medium. The test water containing 5-6 mg F/l and 140-168 mg/l alkalinity was used throughout (56,57). The average fluoride removal capacity of the medium was 484 mg F per litre with 1.15 mg F/l as a mean value of the leakage.

[illegible] treat 91 [illegible] per [illegible] were installed at the Municipal Corporation, Nalgonda and Central Training Institute, Hyderabad, A.P. The plant includes a pressure shell, regeneration tank and a storage reservoir of 4-6 hours capacity. The process in its simplest form consists of passing water through a bed of defluoron-2 medium contained in a cylindrical steel shell to which are attached the necessary pipework and control valves. Immediately adjacent to shell the regeneration tank is located so that the whole installation is compact and is easily maintained. The plants at Nalgonda and CTI were operated through 55 and 40 cycles respectively, by NEERI (58). While the plant at C.T.I., is operating, the plant at Nalgonda is kept idle by Municipality for want of funds.

Based on the extensive trials with the medium, both in the laboratory and in the field, a brochure was prepared (59). The brochure contains the medium characteristics and the design data which are as follows.

Medium characteristics

Bulk density	..	810 kg per m^3
Size	..	0.6-2.0 mm
Voids (approximate)	..	40 per cent
Attritional losses	..	Negligible

Maximum operating service flow rates

(a) 5.0 m^3 per sq.meter of bed area per hour

(b) 5.5 m^3 per hour per m^3 of medium

Wash water treatment

0.15-0.22 m^3 per sq.meter per minute for a maximum duration of 10 minutes.

Regenerant

One bed volume of 4 per cent (w/v) alum solution. A bed volume is equal to the volume of the medium in the unit. The alum solution has a pH between 2.6 and 2.8.

Regenerant contact period with medium

30-40 minutes

Depth of the medium

0.6-1.0 meter

Bicarbonate alkalinity : With raw water fluorides ranging between 8 and 12 mg/l the average defluoridation capacity is 650 mg fluoride per litre of medium. However, because of greater difficulty in fluoride removal at lower concentrations, the capacity of the medium reduces to 480 mg/l of medium, when using a raw water containing between 5 and 7 mg/l of fluoride. These capacities correspond to a raw water alkalinity of 160 mg/l as $CaCO_4$. The capacity of the medium at other alkalinity levels is given in Table 10.

TABLE 10

FLUORIDE REMOVAL CAPACITY*, mg FLUORIDE PER l OF MEDIUM

Bicarbonate alkalinity of the raw water, mg $CaCO_3$/l	Raw water fluoride, mg per litre			
	3-4	5-6	7-8	9-10
160	340	480	560	650
200	300	400	460	530
240	230	300	350	400
300	190	250	270	300
400	140	170	210	250
600	100	120	180	200
900	80	100	120	150

*Based on an average fluoride concentration of 0.6-0.8 mg/l in the treated water.

Hydroxyl alkalinity : The medium can tolerate hydroxyl alkalinity upto about 5 mg/l as $CaCO_3$. The fluoride concentration in the treated water increases with the increase in hydroxyl alkalinity. There is a 30 per cent reduction in the capacity of the medium when hydroxyl alkalinity is 25 mg/l as $CaCO_3$.

Operating and treatment costs

Nearly the whole cost of operating a defluoridation plant is the cost of alum required for regeneration. The actual defluoridation cost depends upon the fluoride and alkalinity content of the raw water. The basis of the calculation is given below.

A. Characteristics of raw water

pH	..	7.0-8.5	
Fluorides, as F	..	a	mg/l
Alkalinity, as $CaCO_3$	..	b	,,
Capacity of the medium corresponding to a & b	..	c	,, fluorides/litre

B. Typical basis for calculation

A pressure type plant with 1.41 M^3 (50 cu.ft) of Defluoron-2 capable of passing 6.8 m^3/hr (1500 gph)

I Capital cost

Plant, piping, valves and regenerating tanks with mixing devices	..	Rs.	14,250/-	
Cost of 1.41 M^3 of medium at the rate of Rs. 2.55	..	Rs.	3,600/-	Rs. 17,850/-

II Depreciation

Plant at 20 % per annum	..	Rs.	2,850/-	
Medium at 33.3 % ,,	..	Rs.	1,200/-	Rs. 4,050/-

III Capital cost of the plant based on five years life expectancy

Cost = Plant + (medium x 1.67)
= Rs. 14,250 + Rs. 3,600 x 1.67
= Rs. 20,262
Say Rs. 20,250/-

C Sample calculation for a mg/l fluorides and b mg/l alkalinity

Capacity of the medium = c mg F per litre of material.
Total fluoride removal capacity of the plant between two successive regenerations = 1,410 c mg

Quantity of water treatable per regeneration

= 1.41 (c/a) M^3

Length of run between regeneration

$$= \frac{1.41\ (c/a)}{6.8} = 0.2\ (c/a)\ \text{hours}$$

Time required per regeneration = 1.5 hours

Number of actual regenerations/day

$$= \frac{24\ a}{(0.2\ c + 1.5\ a)}$$

Quantity of water treatable for 24 hours working, allowing 1.5 hours per regeneration.

$$Q = \frac{24\ a}{(0.2\ c + 1.5\ a)} \times \frac{1.41\ c}{a} = \frac{33.8\ c}{(0.2\ c + 1.5\ )}\ M^3$$

Alum requirement per regeneration = 56 kg

$$\text{Alum requirement per day} = \frac{56 \times 24\ a}{(0.2\ c + 1.5\ a)} = \frac{1344\ a}{(0.2\ c + 1.5\ a)}\ kg$$

Cost of alum @ Re. 0.70 per kg

$$= \frac{0.70 \times 1344\ a}{(0.2\ c + 1.5\ )}\ \text{Rupees} \quad .. \quad (1)$$

$$\text{Depreciation per day} = \frac{\text{Rs. } 4{,}050}{\text{Rs. } 365}$$

$$= \text{Rs. } 11.10 \quad .. \quad (2)$$

Pumping cost of Q cubic metres against a total head of 18.28 M (60 ft) to the over-head reservoir through the plant (including fraction losses and @ Re. 0.10 per unit of power)

$$= \frac{1{,}000 \times Q \times 18.28 \times 10}{102 \times 60 \times 60 \times 100} = \frac{0.168\ c}{(0.2\ c + 1.5\ a)} \quad .. \quad (3)$$

Operational charge (one operator) = Rs. 8.00 per day .. (4)

Cost of treatment per day = K = Charges due to (1) + (2) + (3) + (4)

$$= \frac{941\ a}{(0.2\ c + 1.5\ a)} + 11.10 + \frac{0.168\ c}{(0.2\ c + 1.5\ a)} + 8.00$$

$$= 19.10 + \frac{(941\ a + 0.168\ c)}{(0.2\ c + 1.5\ a)}$$

$$= \frac{(969.65\ a + 3.988\ c)}{(0.2\ c + 1.5\ a)} = \frac{(969.65\ a + 3.988\ c)}{0.2\ c + 1.5\ a}$$

Cost of treatment per M^3 rupees $= \frac{K}{Q}$

$$= \frac{9.69.65\ a + 3.988\ c}{33.8\ c}$$

Capital cost per M^3 rupees $= \frac{20.250}{Q}$

The relationship between raw water fluoride and cost estimates at various raw water alkalinity is given in Table Nos 11 to 14. Table 15 summarises the information on the cost treatment per m^3. In India, most of fluoride bearing waters contain fluoride from 3 to 10 mg/l in the alkalinity range between 160 and 900 mg/l. Such waters can be defluoridated at a cost between 0.39 and 2.10 per m^3. The treatment cost increase appreciably with the alkalinity of the raw water.

Continuous operation of the plant at Central Training Institute for about four years had resulted in the formation of white deposits over the medium and a consequent fall in the defluoridating capacity by about 60 per cent. The volume of the medium had swollen considerably (40 per cent). The ~~volume of the medium was~~ following were the major constituents of the deposits.

Carbonates and hydroxides	..	4,80,000 ppm
Fluorides	..	6,100 ,,
Sulphates	..	6,000 ,,
Aluminium	..	1,73,000 ,,
Calcium	..	24,000 ,,
Magnesium	..	34,000 ,,
Iron	..	11,000 ,,
Acid insoluble (1 : 1 HCl)	..	1,69,700 ,,

The deposits were probably due to inadequate wash after regeneration using one bed volume of 4 % alum solution. The medium was taken out, acid washed and recharged. The plant has since been working.

TABLE 11

DEPENDENCE OF COST OF TREATMENT ON RAW WATER FLUORIDES AND ALKALINITY

Alkalinity in raw water mg $CaCO_3$/l	Quantity of water treatable per regeneration at maximum rate of 6.8 M^3/hr M^3	Quantity of water treatable for 24 hr working allowing 1.5 hr per regeneration M^3	Cost of treatment per M^3 (includes staff, chemicals, depreciation & power) Rs.	Alum requirement per day. kg	Per capita annual cost on the basis of 10 l/capita/day. Rs.
		Raw Water Fluorides 10 mg/l			
160	91.00	150.62	0.56	94	2.04
200	74.28	147.17	0.66	112	2.40
240	56.00	141.47	0.83	143	3.04
300	42.00	134.40	1.10	181	3.92
400	35.00	129.23	1.26	210	4.60
600	28.00	122.18	1.56	248	5.70
900	21.00	112.00	2.11	303	7.69
		Raw water Fluorides 9 mg/l			
160	101.10	152.19	0.51	95	1.88
200	82.04	149.02	0.61	114	2.21
240	62.22	143.74	0.76	146	2.78
300	46.67	137.14	0.99	185	3.57
400	38.89	132.28	1.15	214	4.19
600	31.11	125.61	1.40	254	5.14
900	23.33	115.86	1.84	313	6.71

.. 36

TABLE 12

DEPENDENCE OF COST OF TREATMENT OF RAW WATER FLUORIDES AND ALKALINITY

Alkalinity in raw water mg $CaCO_3$/l	Quantity of water treatable per regeneration of maximum rate of 6.8 M^3/hr M^3	Quantity of water treatable for 24 hr working allowing 1.5 hour per regeneration M^3	Cost of treatment per M^3 (includes staff, chemicals, depreciation & power) Rs.	Alum requirement per day kg.	Per capita annual cost on the basis of 10 l/capita/day Rs.
		Raw Water Fluorides 8 mg/l			
160	112.75	153.80	0.53	96	1.92
200	92.75	150.91	0.62	115	2.25
240	69.99	146.08	0.77	147	2.82
300	52.50	140.00	0.97	189	3.53
400	43.75	135.45	1.21	219	4.42
600	35.00	129.22	1.39	262	5.10
900	26.25	120.00	2.03	324	7.41
		Raw Water Fluorides 7 mg/l			
160	112.00	153.60	0.54	78	1.96
200	92.00	150.79	0.62	93	2.26
240	70.00	146.08	0.79	118	2.87
300	54.00	140.65	0.86	148	3.14
400	42.00	134.40	1.07	181	3.92
600	32.00	126.49	1.23	224	4.50
900	24.00	116.67	1.79	226	6.53

TABLE 13

DEPENDENCE OF COST OF TREATMENT OF RAW WATER FLUORIDES AND ALKALINITY

Alkalinity in raw water mg $CaCO_3$ /l	Quantity of water treatable per regeneration at maximum rate of 6.8 M^3/hr M^3	Quantity of water treatable for 24 hr working allowing 1.5 hour per regeneration M^3	Cost of treatment per M^3 (includes staff, chemicals, depreciation and power) Rs.	Alum requirement per day kg.	Per capita annual cost on the basis of 20 l/capita/day. Rs.
		Raw water Fluorides 6 mg/l			
160	112.00	153.60	0.48	78	1.74
200	93.33	151.01	0.55	92	2.00
240	70.00	146.08	~~0.41~~ 0.69	118	2.52
300	58.33	142.37	0.80	138	2.94
400	39.67	132.83	1.13	190	4.12
600	28.00	122.18	1.55	247	5.66
900	23.33	115.86	1.84	282	6.71
		Raw water Fluorides 5 mg/l			
160	134.40	155.52	0.29	66	1.07
200	112.00	153.60	0.48	77	1.74
240	84.00	149.33	0.59	100	2.17
300	70.00	146.08	0.69	118	2.52
400	47.60	137.63	0.96	164	3.50
600	33.60	128.00	1.31	216	4.79
900	28.00	122.18	1.91	247	6.97

.. 38

TABLE 14

DEPENDENCE OF COST OF TREATMENT OF RAW WATER FLUORIDES AND ALKALINITY

Alkalinity in raw water mg $CaCO_3$/l	Quantity of water treatable per regeneration at maximum rate of 6.8 M^3/hr M^3	Quantity of water treatable for 24 hr working allowing 1.5 hours per regeneration M^3	Cost of treatment per M^3 (includes staff, chemicals, depreciation & power) Rs.	Alum requirement per day kg.	Per capita annual cost on the basis of 25 l/capita/day Rs.
		Raw Water Fluorides 4 mg/l			
160	119.00	154.38	0.45	73	1.66
200	105.00	152.73	0.50	83	1.82
240	80.50	148.61	0.64	105	2.32
300	66.50	145.09	0.72	124	2.63
400	49.00	138.35	0.94	160	3.42
600	35.00	129.23	1.28	218	4.67
900	28.00	122.18	1.55	247	5.66
		Raw Water Fluorides 3 mg/l			
160	153.67	157.57	0.37	56	1.35
200	140.00	156.28	0.40	64	1.47
240	107.33	153.03	0.49	81	1.79
300	88.67	150.21	0.57	96	2.08
400	65.33	144.73	0.73	126	2.67
600	46.56	137.14	0.99	166	3.57
900	37.33	131.12	1.19	199	4.35

TABLE 15

RELATIONSHIP BETWEEN RAW WATER FLUORIDE AND COST ESTIMATE*

Fluoride concentration in raw water. mg/l	Length of run between regenerations hours	Quantity of water treatable per regeneration of maximum rate of 6.8 M^3/hr M^3	Cost of treatment per M^3 (including staff, chemicals, depreciation, power etc.) Rs.	Per capita annual cost on the basis of 10 lpcd. Rs.
3	5.3–22.7	37.33–158.67	0.37–1.19	1.35–4.35
4	4.0–17.0	28.00–119.00	0.45–1.55	1.66–5.66
5	4.0–19.2	28.00–134.40	0.29–1.91	1.06–6.97
6	3.3–16.0	23.33–112.00	0.47–1.87	1.73–6.71
7	3.4–16.0	24.00–153.60	0.53–1.79	1.95–6.53
8	3.9–16.3	26.75–113.75	0.52–2.03	1.92–7.40
9	3.3–14.4	23.33–101.11	0.51–1.83	1.87–6.71
10	3.0–13.0	21.00–91.00	0.55–2.10	2.04–7.69

* Depends on the alkalinity of raw water which varies between 160 to 900 mg/l as $CaCO_3$.

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Nalgonda Technique

Though defluoron-2 process was successful in removing fluorides, the regeneration and maintenance of the plant required skilled operation which may not be readily available. In order to overcome this problem a new method has been developed by NEERI (60). The method is so simple and adaptable that even illiterate persons can make use of it. Incidentally, the cost of defluoridation has also been brought down considerably.

The new method has been named ' Nalgonda Technique ' and involves the addition of two readily available chemicals. The process comprises treatment of water with sodium aluminate or lime and filter alum in sequence followed by flocculation, sedimentation and filtration. These operations are simple and familiar to ~~engineering~~ engineers and it is hoped that this technique of defluoridation will soon be applied to endemic fluorosis areas either on individual basis or a community level. Lime which is far cheaper is recommended instead of sodium aluminate. Boruff (25), Scott, et. al (61) and Kempf (62) studied the use of filter alum for reduction of fluoride from drinking water but the method, however, was not popularised.

Domestic treatment is further simplified to enable an individual to adapt the process to his requirements. Any container of 20-60 litres is suitable for this purpose. A tap 3-5 cm above the bottom of the container is useful to withdraw the treated water but is not essential. The raw water taken into the container is mixed with adequate amounts of lime and alum . Bleaching powder for disinfection can be added simultaneously with lime and alum. The quantity required was found to depend on dissolved solids, alkalinity and fluorides in the raw water.

Table 21 gives the dose in mg of filter alum per litre of water. The lime dose is 1/20th of the alum.

Lime powder and bleaching powder are sprinkled first and mixed well with the water. Alum solution is then poured and the water is stirred for ten minutes. The contents are settled for one hour and the clear water is withdrawn either through the tap or decanted slowly without disturbing the sediment. The fluoride concentration in the settled water will be within the allowed permissible limits.

With domestic treatment there is no capital investment necessary and the cost of treatment is all that of the cost of chemicals only.

Experimental work

Considerable work was done by NEERI on Nalgonda Technique for defluoridation. The study was grouped under the following categories :

i) Laboratory investigation
ii) Field work
iii) Plant work.

Laboratory investigations consisted of evaluation of alum dose required for waters with varying concentrations of fluoride, alkalinity, ionic strength. The effect of free available chlorine, sulphate, calcium hardness, organic matter, nitrates, polyphosphates and silicates were studied.

The field work was designed to demonstrate the usefulness and simplicity of the technique. It includes (a) experiments in buckets, (b) experiments in drums and (c) pilot plant studies. While (a) and (b) are fill and draw type batch experiments, (c) is a continuous process. The batch experiments were carried out using well waters from different sources and the settled waters was tested for fluoride.

The details of the experimental work was given by Nawlakhe et. al (60). Laboratory investigations were carried out by jar tests using sodium aluminate (later replaced by lime) and filter alum. The following sets of experiments were carried out (Table 16).

alum fluoride concentration was reduced to 0.9 mg F/l with pH 6.7 and alkalinity 56 mg/l $CaCO_3$ which indicates saving of alum by 1,500 mg/l. The experiments on fluoride concentration lower than 8 mg/l have not given encouraging results by split treatment. Waters having fluoride more than 10 ppm can be economically treated with split (two stage) treatment.

Laboratory studies on the effect of water quality on the removal of fluorides

The removal of fluoride by Nalgonda Technique was found to be independent of Ca^{++}, Mg^{++}, Na^{+}, K^{+}, Cl^{-}, $SO_4^{=}$, NO_3^{-} and free residual chlorine in the test water. The presence of the following did not adversely affect the removal of fluoride sulphates 50 to 550 mg SO_4/l, Calcium 100 to 500 mg Ca/l, Chlorides 178 to 890 mg Cl/l and chlorine upto 10 mg/l. Certain laboratories in the country speculated interference from soluble silica, organic matter and phosphates, even in trace quantities and consequent reduction in fluoride removal by this technique. To verify this, further laboratory experiments were conducted using polyphosphates, silicates and organic matter.

Polyphosphates :- Sodium hexa-meta-phosphate, sodium pyro-phosphate, sodium tri-polyphosphate were used (1-5 mg P/l) and the fluoride removal was not affected.

Silicates :- Varying doses of sodium meta silicate (5-60 mg SiO_2 /l) were tested. It is observed that silicates has adversex effect on the defluoridation. The residual fluoride concentration was 1.10, 1.45, 2.05 and 2.70 mg/l at 0, 20, 40 and 60 mg/l silica levels respectively when 5.1 mg F/l of fluoride water was treated.

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TABLE 17

REMOVAL OF FLUORIDE BY ALUM

(Test water alkalinity - 80 mg $CaCO_3$ /l)

Dose, mg Al/l	pH and fluorides in treated water							
	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l
0	7.8	2.05	7.8	2.95	7.8	3.90	7.8	4.70
0.7	7.6	1.95	7.6	2.85				
1.4	7.4	1.90	7.4	2.75	7.4	3.60	7.3	4.40
2.1	7.3	1.75	7.2	2.65				
2.8	7.1	1.70	7.1	2.55	7.2	3.25	7.1	4.05
3.5	7.0	1.65	7.0	2.45				
4.2	6.9	1.55	6.9	2.30	7.1	2.90	7.0	3.75
4.9	6.8	1.45	6.9	2.20				
5.6	6.9	1.35	6.8	2.05	7.0	2.65	6.8	3.40
6.3	6.8	1.25	6.8	1.95				
7.0	6.7	1.15	6.7	1.75	6.3	2.40	6.6	3.15
7.7	6.6	1.10	6.7	1.70				
8.4			6.7	1.65	6.6	2.30	6.5	2.95
9.8			6.6	1.55	6.4	2.20	6.3	2.85
11.2			6.4	1.50	6.3	2.10	6.3	2.75

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TABLE 18

REMOVAL OF FLUORIDE BY ALUM

(Test water alkalinity - 125 mg $CaCO_3$ /l)

Dose, mg Al/l	pH and fluorides in treated water									
	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg
0	7.7	2.15	7.7	3.10	7.7	4.10	7.9	4.90	7.9	5.80
1.4	7.3	1.95	7.5	2.90	7.5	3.90				
2.8	7.2	1.80	7.3	2.75	7.4	3.70	7.4	4.40	7.5	5.20
4.2	7.0	1.65	7.2	2.60	7.2	3.45				
5.6	6.9	1.55	7.1	2.40	7.1	3.20	7.3	3.90	7.1	[illegible]
7.0	6.8	1.40	7.0	2.15	7.0	2.95				
8.4	6.7	1.25	6.9	2.00	6.9	2.70	7.1	3.45	6.9	[illegible]
9.8	6.6	1.10	6.8	1.80	6.8	2.55				
11.2	6.6	1.00	6.7	1.70	6.7	2.40	6.9	2.90	6.8	3.65
12.6	6.5	0.93	6.6	1.60	6.6	2.55				
14.0	6.4	0.86	6.6	1.45	6.5	2.10	6.7	2.55	6.6	3.35
15.4	6.3	0.79	6.5	1.35	6.4	2.00				
16.8			6.5	1.15	6.5	1.80	6.5	2.35	6.5	3.00
19.6							6.4	2.30	6.3	[illegible]

TABLE 19

REMOVAL OF FLUORIDE BY ALUM

(Test water alkalinity - 200 mg $CaCO_3$ /l)

Dose, mg Al/l	pH and fluorides in treated water									
	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l
0	8.6	2.30	8.6	3.20	8.6	4.10	8.6	5.10	8.6	6.30
2.6	8.0	2.20	8.0	3.05	7.9	3.90	7.9	4.90	8.0	6.10
5.6	7.6	2.05	7.6	2.75	7.7	3.65	7.6	4.60	7.7	5.60
8.4	7.3	1.80	7.3	2.35	7.4	3.10	7.4	4.10	7.3	5.00
11.2	7.1	1.55	7.2	2.05	7.2	2.70	7.2	3.50	7.2	4.40
14.0	7.0	1.25	7.0	1.70	7.1	2.30	7.0	3.00	7.0	2.80
16.8	6.8	1.00	6.8	1.45	6.9	1.90	6.9	2.60	6.8	3.30
19.6	6.7	0.68	6.7	1.25	6.8	1.65	6.7	2.25	6.7	2.80
22.4	6.6	0.60	6.6	1.10	6.7	1.50	6.6	2.10	6.6	2.65
25.2	6.5	0.52	6.5	0.93	6.6	1.35	6.5	1.90	6.5	2.40
28.0	6.3	0.45	6.4	0.90	6.4	1.25	6.4	1.70	6.3	2.20
30.8	6.2	0.42	6.2	0.86	6.2	1.20	6.2	1.65	6.2	2.20

TABLE 20

REMOVAL OF FLUORIDE BY ALUM

(Test water alkalinity ~ 310 mg $CaCO_3$ /1)

Dose, mg Al/1	pH and fluoride in treated water													
	pH	mg F/1	pH	mg F/1	pH	mg F/1	pH	mg F/1	pH	mg F/1	pH	mg F/1	pH	mg F/1
0	8.90	2.25	8.90	3.20	8.90	[illegible]	9.0	5.10	8.80	6.0	8.4	8.0	8.4	10.20
4.2	8.5	2.15	8.5	3.10	8.4	4.0	8.5	5.0	8.3	5.8	7.9	7.60	8.0	9.80
8.4	7.9	1.90	8.0	2.85	8.0	3.65	[illegible]	4.50	7.8	5.1	7.7	7.20	7.7	9.00
12.6	7.6	1.60	7.6	2.35	[illegible]	[illegible]	[illegible]	[illegible]	7.5	4.2	7.5	6.40	7.5	8.10
16.8	7.3	1.35	7.3	1.95	7.4	[illegible]	[illegible]	[illegible]	7.3	3.65	7.2	5.70	7.3	7.20
21.0	7.2	1.10	7.2	1.35	[illegible]	[illegible]	[illegible]	[illegible]	7.2	3.10	7.1	5.00	7.2	6.45
25.2	6.9	0.70	7.0	1.25	[illegible]	[illegible]	[illegible]	[illegible]	7.1	2.50	7.0	4.30	7.1	5.70
29.4	5.7	0.54	6.9	1.00	[illegible]	[illegible]	[illegible]	[illegible]	6.8	2.15	6.9	[illegible]	6.9	5.00
[illegible]	5.6	0.43	6.7	0.84	6.7	[illegible]	[illegible]	1.45	6.7	1.80	6.8	3.30	6.8	4.40
[illegible]	5.5	0.35	6.7	0.71	6.7	[illegible]	[illegible]	1.25	6.5	1.60	6.7	2.90	6.7	4.00
[illegible]	5.4	0.27	6.5	0.62	6.5	0.80	[illegible]	1.10	6.4	1.45	6.6	2.60	6.6	3.65
[illegible]	[illegible]	[illegible]	6.3	0.54	6.5	0.70	6.5	0.98	6.3	1.30	6.4	2.40	6.4	3.40

TABLE 21

REMOVAL OF FLUORIDE BY ALUM

(Test water alkalinity of 400 mg $CaCO_3$ /1)

Dose, mg Al/1	pH and fluoride in treated water													
	pH	mg F/1	pH	mg F/1	pH	mg F/1	pH	mg F/1	pH	mg F/1	pH	mg F/1	pH	mg F/1	[illegible]
0	8.6	2.20	8.6	3.20	8.6	4.20	8.7	5.20	8.7	6.30	8.6	8.00	8.7	10.20	400
5.6	7.9	2.00	7.9	2.90	8.1	3.75	8.1	4.70	8.1	6.00	8.3	7.30	8.3	9.60	360
11.2	7.5	1.70	7.5	2.45	7.7	3.10	7.7	4.00	7.6	5.20	8.2	6.50	8.2	8.70	33[illegible]
16.8	7.3	1.40	7.3	2.00	7.4	2.50	7.6	3.30	7.5	4.20	8.1	5.70	8.1	7.50	304
22.4	7.1	1.10	7.1	1.50	7.2	2.05	7.4	2.55	7.3	3.40	8.0	4.80	8.0	6.50	288
28.0	7.0	0.75	7.0	1.20	7.1	1.60	7.1	2.10	7.2	2.65	7.9	4.10	7.9	5.50	[illegible]
33.6	6.8	0.54	6.8	0.85	7.0	1.30	7.0	1.65	7.0	2.65	7.7	3.35	7.8	4.75	[illegible]
39.2	6.7	0.42	6.7	0.63	6.8	0.92	6.8	1.30	6.9	1.75	7.6	2.75	7.6	4.00	[illegible]
44.8	6.6	0.32	6.6	0.49	6.7	0.63	6.7	1.05	6.7	1.45	7.4	2.35	7.4	3.40	188
50.4	6.5	0.26	6.5	0.38	6.7	0.58	6.6	0.80	6.7	1.20	7.3	2.05	7.3	3.00	144
56.0	6.3	0.23	6.4	0.32	6.5	0.51	6.5	0.72	6.5	1.15	7.1	1.85	7.1	2.70	13[illegible]
61.6	6.2	0.21	6.2	0.29	6.4	0.51	6.5	0.64	6.4	0.92	6.9	1.70	6.9	2.50	10[illegible]

TABLE 22

REMOVAL OF FLUORIDE BY ALUM

(Test water alkalinity 500-510 mg $CaCO_3$/l)

Dose, mg Al/l	pH and fluoride in treated water														Residual alkalinity, mg $CaCO_3$/l
	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	
0	9.4	2.3	9.2	3.10	9.2	4.30	9.2	5.20	9.2	6.10	8.8	8.10	8.8	10.20	510
7.0	8.9	2.10	8.7	2.90	8.7	4.00	8.7	4.90	8.7	5.80	8.0	7.30	8.1	9.20	484
14.0	8.5	1.85	8.1	2.60	8.1	3.70	8.1	4.50	8.1	5.20	7.7	6.20	7.7	7.80	448
21.0	8.3	1.55	7.7	2.20	7.8	2.90	7.8	3.70	7.8	4.10	7.4	6.10	7.4	6.20	408
28.0	8.1	1.15	7.4	1.75	7.5	2.15	7.5	2.85	7.5	3.00	7.2	3.95	7.2	5.00	364
35.0	7.9	0.84	7.2	1.25	7.3	1.55	7.3	2.10	7.3	2.40	7.0	4.15	7.0	4.00	328
42.0	7.7	0.62	7.0	0.92	7.1	1.15	7.1	1.60	7.0	1.75	7.0	2.40	6.9	3.25	288
49.0	7.6	0.49	6.8	0.68	6.9	0.90	6.9	1.15	6.9	1.35	6.8	1.95	6.8	2.00	248
56.0	7.3	0.36	6.7	0.51	6.7	0.97	6.7	0.94	6.7	1.10	6.7	1.60	6.6	2.15	208
63.0	7.1	0.32	6.5	0.40	6.5	0.56	6.5	0.77	6.5	0.92	6.5	1.35	6.5	1.85	176
70.0	7.0	0.25	6.4	0.35	6.4	0.50	6.4	0.65	6.4	0.84	6.4	1.15	6.4	1.60	156
77.0	6.8	0.21	6.3	0.31	6.3	0.41	6.3	0.68	6.3	0.78	6.3	1.10	6.2	1.50	120

[illegible]

[illegible]

([illegible] water alkalinity = [illegible] mg $CaCO_3$ /l)

Dose, mg Al/l	pH and fluoride in treated water: pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	Residual alkalinity mg $CaCO_3$
[illegible]	9.1	1.35	9.1	[illegible]	[illegible]	[illegible]	[illegible]	5.20	8.9	5.40	8.9	8.60	8.9	10.20	600
[illegible]	8.3	1.35	[illegible]	2.30	[illegible]	[illegible]	[illegible]	4.30	8.6	[illegible]	8.6	7.70	8.2	9.10	554
[illegible]	7.8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.8	4.20	8.5	4.90	8.3	6.70	7.7	7.50	476
[illegible]	7.4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.15	[illegible]	[illegible]	[illegible]	[illegible]	7.4	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.2	2.25	8.1	[illegible]	[illegible]	[illegible]	7.1	4.60	380
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.1	1.65	7.9	2.25	7.9	3.10	7.0	3.60	340
[illegible]	6.9	0.51	[illegible]	[illegible]	[illegible]	[illegible]	6.9	1.20	7.8	1.75	7.8	2.40	6.8	2.80	296
[illegible]	6.5	0.37	6.8	0.38	[illegible]	[illegible]	6.8	0.92	7.7	1.35	7.6	1.90	6.7	2.25	254
87.2	[illegible]	0.23	5.7	[illegible]	5.7	[illegible]	6.6	0.74	7.6	1.10	7.5	1.55	6.6	1.85	210
[illegible]	[illegible]	0.28	5.6	[illegible]	[illegible]	[illegible]	6.5	0.57			7.3	1.30	6.4	1.55	180
89.0	6.3	0.25	[illegible]	0.33	[illegible]	[illegible]	6.4	0.51			6.9	1.15	6.3	1.40	140
92.4	[illegible]	[illegible]	6.2	[illegible]	[illegible]	[illegible]	[illegible]	0.48			5.8	1.10	6.1	1.25	[illegible]

TABLE 24

REMOVAL OF FLUORIDE BY ALUM

(Test water alkalinity 820 mg $CaCO_3$ /l)

Dose, mg Al/l	pH and fluoride in treated water												Residual alkalinity mg $CaCO_3$/l
	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	
0	8.9	2.00	9.0	2.90	8.9	4.00	8.9	5.20	9.0	6.20	8.9	8.30	9.0	10.40	800
11.2	8.2	1.70	8.5	2.60	8.5	3.65	8.3	4.30	8.7	5.80	8.6	7.60	8.8	8.80	740
22.4	7.7	1.30	8.0	1.95	8.1	3.15	7.6	3.30	8.3	4.60	8.3	6.20	8.7	7.40	672
33.6	7.5	0.94	7.7	1.35	8.0	2.30	7.5	2.90	7.9	3.40	7.7	4.70	8.6	5.70	600
44.8	7.3	0.64	7.4	1.00	7.6	1.35	7.2	2.40	7.8	2.55	7.7	3.60	8.4	4.30	536
56.0	7.1	0.44	7.3	0.76	7.2	0.96	7.1	1.65	7.6	1.85	7.6	2.60	8.1	3.30	476
67.2	7.0	0.37	7.0	0.59	6.9	0.72	6.9	1.20	7.5	1.40	7.3	2.00	7.8	2.55	408
78.4	6.9	0.30	6.9	0.42	6.8	0.54	6.8	0.94	7.1	1.10	7.1	1.55	7.5	2.00	348
89.6	6.7	0.25	6.7	0.34	6.6	0.43	6.6	0.74	7.0	0.85	6.8	1.20	7.3	1.65	288
100.8	6.4	0.22	6.4	0.31	6.4	0.35	6.5	0.59	7.9	0.71	6.7	0.98	7.0	1.35	244
112.0	6.1	0.20	6.2	0.29	6.3	0.32	6.4	0.53	6.8	0.61	6.6	0.90	6.9	1.15	104
123.2	5.9	0.20	6.0	0.28	6.2	0.31	6.3	0.50	6.7	0.55	6.6	0.78	6.8	1.05	60

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TABLE 25

REMOVAL OF FLUORIDE BY ALUM

(Test water alkalinity 1070 mg $CaCO_3$ /l)

Dose, mg Al/l	Test water alkalinity 1070 mg CaCO														Residual alkalinity mg $CaCO_3$/l
	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	pH	mg F/l	
0	8.9	2.10	8.9	3.30	8.8	4.10	8.8	5.30	8.8	5.80	8.8	7.80	8.8	10.50	1070
14	8.1	1.90	8.1	2.85	8.1	3.80	8.1	4.70	8.3	5.20	8.3	7.10	8.1	9.50	976
28	7.7	1.45	7.6	2.10	7.6	2.90	7.6	3.40	7.9	4.00	7.9	5.40	7.6	8.00	876
42	7.3	1.00	7.3	1.45	7.3	2.05	7.4	2.50	7.6	2.90	7.6	3.90	7.4	6.20	804
56	7.1	0.70	7.1	1.05	7.1	1.45	7.1	1.75	7.4	2.15	7.4	2.80	7.1	4.60	720
70	7.0	0.52	7.0	0.80	7.0	1.05	7.0	1.25	7.2	1.55	7.2	2.10	7.0	3.55	652
84	6.8	0.40	6.8	0.56	6.8	0.76	6.9	0.92	7.1	1.15	7.1	1.60	6.9	2.15	568
98	6.7	0.35	6.7	0.43	6.6	0.59	6.7	0.73	6.9	0.92	6.9	1.15	6.8	1.65	492
112	6.6	0.30	6.6	0.35	6.5	0.45	6.6	0.54	6.9	0.74	6.8	0.94	6.7	1.30	420
126	6.5	0.24	6.4	0.29	6.4	0.39	6.5	0.47	6.7	0.62	6.8	0.76	6.6	1.10	352
140	6.3	0.20	6.2	0.25	6.2	0.31	6.3	0.38	6.6	0.50	6.6	0.65	6.4	0.92	288
154	6.2	0.18	6.1	0.21	6.1	0.28	6.2	0.35	6.5	0.44	6.4	0.56	6.3	0.82	224

TABLE [illegible]

APPROXIMATE ALUM DOSE (mg Al/l) REQUIRED TO OBTAIN EXCESSIVE (E) AND PERMISSIVE (P) LIMITS OF FLUORIDE IN WATER AT VARIOUS TEST WATER ALKALINITY AND FLUORIDE LEVELS

Test water fluorides, mg F/l	Test water alkalinity expressed as mg $CaCO_3$ per litre: 80		125		200		[illegible]		400		510		600		820		1070	
	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P
2	0	8	0	[illegible]	0	[illegible]	0	[illegible]	[illegible]	24	[illegible]	[illegible]	0	31	0	36	0	40
3	6	**	9	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	24	39	27	40	29	45	33	59
4	11		[illegible]	**	16	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	30	43	31	46	37	53	43	72
5	*		[illegible]		[illegible]	**	[illegible]	[illegible]	[illegible]	46	36	53	37	55	50	68	51	[illegible]
6			[illegible]		[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	46	72	54	92	[illegible]	[illegible]
8					[illegible]		[illegible]	**	[illegible]	**	48	76	57	86	67	100	72	[illegible]
10							*		*		59	**	64	**	78	116	89	[illegible]

To obtain alum dose in mg/l, multiply the values of mg Al/l shown in the table by a factor 13.

The dose can serve as a guideline.
Stars indicate that it is not possible to reduce the fluoride to the corresponding limits. Such conditions comprising high fluoride and low alkalinity are not usual in India. If at all, such condition exists, the alkalinity of the test water will have to be increased by lime and then giving the requisite dose of alum.

* Not possible to obtain excessive limit of 2 mg F/l

** Not possible to obtain permissive limit of 1 mg F/l

Organic matter :- There is no adverse effect of dissolved organic matter (4 to 20 mg/l permanganate value 4 hrs room temperature) on the removal of fluorides from water.

Fluoride material balance

In the Nalgonda Technique, the fluoride is removed along with the floc which settles at the bottom of the container. The removal of fluoride is usually calculated as the difference between the concentration of fluoride in the test water and treated water. In order to establish these removals it was thought worthwhile to estimate fluoride in the settled sludge and supernatant water to establish a material balance of fluoride.

Detailed experiments were carried out using the following test waters.

Fluorides, mg F/l	2.05	3.80	5.70	8.10	11.20
Alkalinity, mg/l	210	400	570	800	1010

The results given by Nawlakhe (63). The fluoride is removed along with the sludge which is settled at the bottom. When this removal is added to the fluoride concentration in the treated water, the sum is almost equal to the fluoride content in the test water. The statistical evaluation indicates that the fluoride material balance is significant thereby confirming fluoride removal in the system of Nalgonda Technique for Defluoridation of Water.

Field studies

An important objective of the field studies is to verify the laboratory findings under the field conditions. Hence, series of bucket experiments were conducted using fluoride water collected from the wells in Rajasthan and Andhra Pradesh. In these studies, 40 l of water was treated with requisite amount of chemicals, stirred for ten minutes and settled for one hour. The supernatant was

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withdrawn either through the tap or by decantation. The thick sediment is not easily disturbed and was discarded. The supernatant was clear with turbidity below 5 units and was tested for pH, alkalinity and residual fluorides. The data from a few representative wells is tabulated in Table 27. The treated water was used for consumption and there were no adverse comments. Domestic treatment is thus, simplified to the utmost to enable an individual to adopt the technique to suit his requirements.

TABLE 27

BUCKET EXPERIMENTS

No.	Dose, mg Al/l	Raw water			Treated water		
		pH	alkalinity, mg $CaCO_3$/l	fluorides, mg F/l	pH	alkalinity, mg $CaCO_3$/l	fluorides, mg F/l
1	20	7.2	236	2.05	6.9	115	1.10
2	22	8.1	330	2.20		214	0.40
3	32	7.9	240	2.60	6.9	66	0.41
4	32	6.9	240	2.60	6.1	60	0.50
5	32	7.6	240	2.10	6.1	60	1.05
6	28	7.9	540	2.95	6.9	360	0.98
7	32	7.8	270	3.70	6.9	70	1.10
8	32	7.6	480	3.30		280	1.09
9	45	8.2	420	4.70		180	0.50
10	48	7.7	454	5.00		160	1.20
11	68	7.8	710	5.90	6.4	300	0.74
12	72	7.8	500	6.90		50	1.20
13	72	7.7	580	7.80		110	1.10
14	90	8.2	690	13.60		100	1.90
15	90	8.0	710	14.20		130	2.00

The extension work carried out during the various field visits was on the following lines.

1. Meetings with local leaders and officials to explain the salient features of the defluoridation technique.

2. Popular talks at largely attended meetings highlighting the usefulness of the process.

3. Demonstration of the process at the public meetings in glass jars and buckets.

4. Demonstration of the technique of preparation of alum tablets at the public meetings.

5. Making selected public participate in the demonstrations, asking them to re-demonstrate what they had seen and learnt to those present at the meeting.

6. Creating awarness among public by requesting a few at random to go around to check whether the residents correctly understood the procedure of defluoridation.

7. Inviting medical practioners to explain the process at each village.

8. Analysis of raw and treated water samples on the spot for conductivity, pH, alkalinity, total hardness, calcium hardness and fluorides.

9. Fixing doses of bleaching powder, lime and alum required for each source of raw water on the basis of analysis of the samples.

10. Making public conscious of the water sources that are otherwise unsuitable for potable purposes; those wells that show dissolved solids beyond 3,000 mg/l were suggested unsuitable, save exceptional circumstances where no alternatives were available.

11. Field preparation and distribution of filter alum tablets; over 30,000 tablets of assorted sizes were prepared and distributed to public in various villages.

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Economics

On the basis of the field work, the following two examples are pertinent to individual treatment of fluoride water in villages.

Example 1 : Human beings alone

Basis :

Fluorides	..	8.8 mg F/l
Alkalinity	..	600 mg/l as $CaCO_3$
Alum dose	..	1.1 g/l
Lime dose	..	50 mg/l

Family : Ten members @ five litres/capita/day

Total water required 10 x 5 = 50 l/day

Water requirement per annum	..	18,250 l
Total alum required	..	20 kg
Total lime required	..	1 ,,
@ Re. 0.70 per kg alum and Re. 0.20 per kg lime total cost per annum	..	Rs. 14.20
i.e., cost/(capita) (annum)	..	Rs. 1.42

Example 2 : Human beings and cattle

Basis :

Family - 10 members @ 5 lpcd	..	50 litres
Cattle - 10 heads @ 30 ,,	..	300 ,,
Water requirement per day	..	350 ,,
Total water requirement/annum	..	128 m^3
Fluoride content in water	..	6 mg F/l
Alkalinity, as $CaCO_3$	..	600 mg/l
Alum dose, mg/l	..	950 ,,
Lime dose, ,, (1/20th)	..	48 ,,
Cost of alum per kg	..	Rs. 0.70
Cost of lime ,, ,,	..	Rs. 0.20

Annual requirement of chemicals for the example

Alum	..	1,28,000 x 950 mg
	=	122 kg.
Lime	..	122/20
	=	6 kg.

Annual cost for 10 members and 10 cattle heads

= (122 kg x Re. 0.70 per kg + 6 kg x Re. 0.20 per kg)

= Rs. 86.60.

or Rs. 7.22 per month

About 6/7th of the cost is for cattle and 1/7th for the human beings.

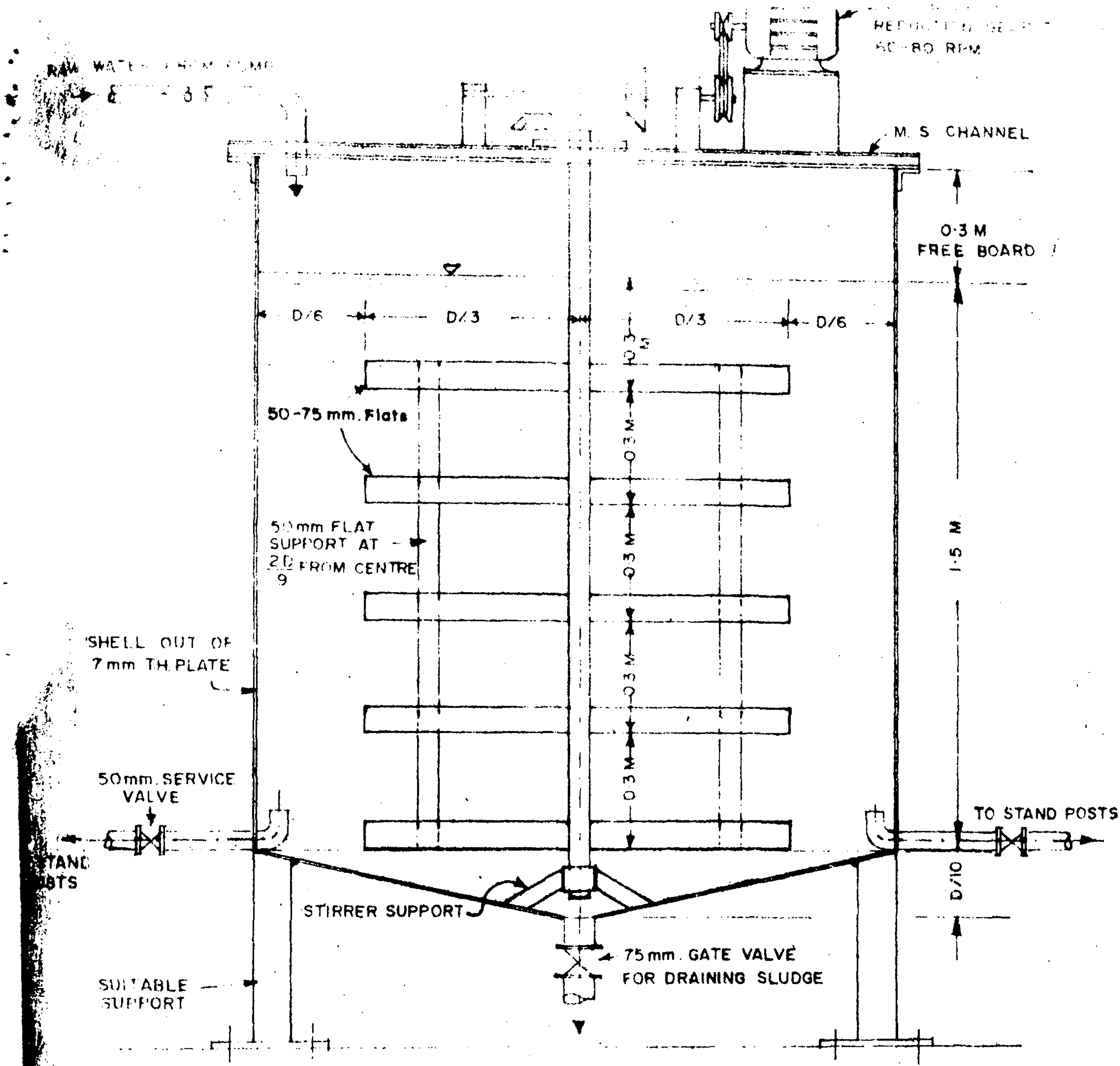

FIG-1 FILL AND DRAW TYPE DEFLUORIDATION PLANT.

BASIS: 15 lpcd DOMESTIC WATER.

Fill and Draw Type Defluoridation Plant for Small Community

For communities with a population ranging from 200-2000 a defluoridation plant of fill and draw type as shown in the FIG. 1 is recommended. The plant consists of a hopper-bottom cylindrical tank with a depth of 2 M. The diameter varies depending upon the quantity of water to be treated. It has a stirring mechanism which can be either hand operated or power driven.

Raw water is pumped to the unit and required quantity of bleaching powder, lime and alum are added as per Table 28. The contents are stirred thoroughly for ten minutes and allowed to settle for 1-2 hrs. The settled sludge is discarded and defluoridated supernatant is supplied through stand-posts. Among the notable features of this process are the following : With a pump of adequate capacity the entire operation can be completed in about four hours time and at least three batches of defluoridated water can be obtained in a day. The accessories needed are few and these are easily available. These include small buckets for dissolving alum, preparation of lime slurry, bleaching powder and a balance. The plant can be located in the open with precautions to cover the motor. A semi-skilled operator can perform the function independently. Plant dimensions for population range from 200 to 2,000 are given in Table 29.

TABLE 28

DOSES OF FILTER ALUM REQUIRED IN NALGONDA TECHNIQUE FOR DEFLUORIDATION

Filter alum (16-17 %) alumina required to obtain excessive and permissive values of fluor[illegible] treated water at various raw water alkalinity and fluoride levels. The doses (mg/l) are [illegible] and can serve as a guideline. The values with an underline are not generally recommended. [illegible] required is 1/20th of filter alum.

Raw water fluorides, mg F/l	80		125		200		310		400		510		600		820	
	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	
2	0	104	0	143	0	221	0	2[illegible]3	0	312	0	351	0	403	0	44[illegible]
3	78	*	117	221	156	299	200	351	260	403	312	507	351	520	[illegible]77	56[illegible]
4	143		195	*	208	403	286	416	299	468	390	559	403	598	481	6[illegible]
5	*		247		286	*	338	507	377	598	468	689	471	715	650	
6			*		403		390	611	455	715	520	780	598	936	702	
8					*		598	*	663	*	624	988	741	1118	871	[illegible]
10							*		*		767	*	832	*	1014	[illegible]

E - excessive limit, 2 mg F/l. P - permissive limit, 1 mg F/l * Not possible to attain the limit at th[illegible] alkalinity.

Conditions comprising high fluoride and low alkalinity are not usual in India. When [illegible] conditions prevail the alkalinity of the raw water can be increased by lime.

FIG No [illegible] Plant

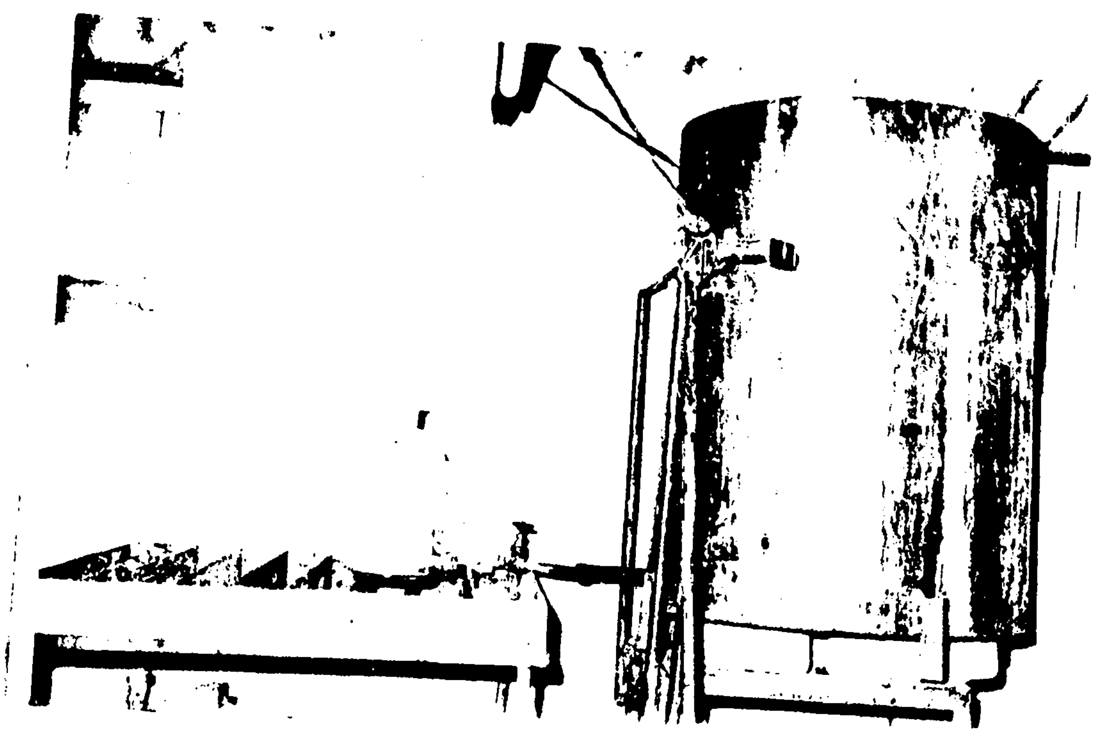

FIG 3

[illegible] flocculation
Pilot Plant.

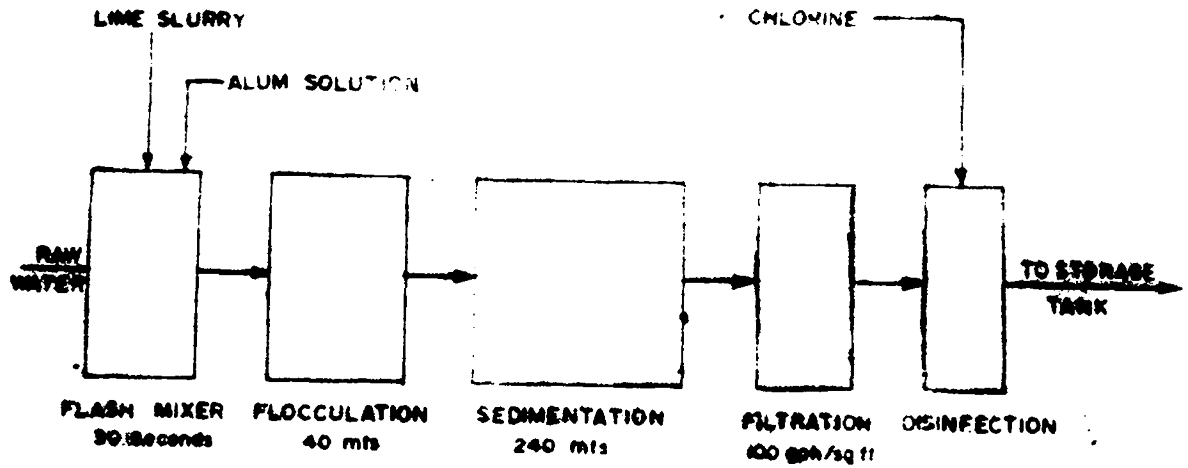

Fig. 4 — Flowsheet for Defluoridation of water by Nalgonda Technique

TABLE 29

PLANT DIMENSIONS FOR POPULATION RANGE FROM 200 TO 2000

Population	Volume M^3	Diameter (D) M	Water Depth M	Free Board M	Depth sludge cone M	Shaft Dia	H.P. required
2000	30.0	5.0	1.5	0.3	0.50	50 mm	5.0
1500	22.5	4.5	1.5	0.3	0.45	,,	5.0
1000	15.0	3.6	1.5	0.3	0.36	,,	4.0
500	7.5	2.5	1.5	0.3	0.25	,,	3.0
200	3.0	1.7	1.5	0.3	0.17	,,	3.0

Pilot Plant Studies

The clariflocculator was operated both in field as well as in laboratory. The operation in laboratory FIG. 2 & 3 lasted several days and was designed to compile information on the performance of the plant under varying conditions of test water fluorides and alkalinity. The test water composition was adjusted by adding sodium bicarbonate and sodium fluoride to the tap water.

Operation of the Plant Stopping the Paddles

The test water and chemicals are introduced simultaneously into a pipe leading to the flocculator. Data was collected for continuous runs lasting over 30 hours after stabilization. The performance is summarised in Table 30. The alkalinity and sulphate concentration in the treated water fluctuated considerably; they were 64-188 mg $CaCO_3$ /l and 160-260 mg SO_4 /l respectively. The fluoride could not be brought down to the permissible 1 mg F/l possibly due to inadequate mixing of test water with reactants.

Operation of the Plant Using the Paddles

The operation of the plant was continued by commissioning the flocculation paddles to observe improvement in fluoride reduction as a result of adequate mixing. Data was collected for another 30 hours and is shown in Table 31. The test water characteristics remained the same and the fluorides in the treated water varied between 0.80 and 0.96 mg F/l indicating improvement [illegible] removal with mixing. Effective mixing is, therefore, essential to achieve proper reduction in fluorides.

The field studies with the plant operated at four places confirmed the laboratory findings. The field trials were on a test water containing 2.0-5.4 mg F/1.

TABLE 30

PERFORMANCE OF PLANT WITHOUT THE PADDLES

Test water fluoride .. 3.3-4.3 mg F/1

Test water alkalinity .. 260-300 mg $CaCO_3$ /1

Time, hrs	Alum dose, mg Al/1	pH of the treated water	Fluorides in treated water, mg F/1	Quantity of treated water, litres
5	36	6.4	1.30	780
7	33	6.6	1.60	1005
12	32	7.0	1.70	1980
15	37	7.1	1.60	2535
17	37	6.7	1.70	3085
23	23	7.2	[illegible].10	4325
25	39	7.4	1.90	4740
29	41	6.9	1.40	5100

TABLE 31

PERFORMANCE OF PLANT WITH THE PADDLES

Test water .. 3.3-4.3 mg F/1

Test water alkalinity .. 260-300 mg $CaCO_3$ /1

Time,	Alum dose, mg Al/1	pH of the treated water	Fluorides in treated water, mg F/1	Quantity of treated water, litres
3	27	6.8	1.10	640
6	33	6.2	0.80	1100
7	35	6.1	0.77	1250
9	39	5.9	0.94	1790
13	39	6.2	0.81	2510
16	42	6.0	0.84	3060
20	43	6.0	0.98	3950
25	43	6.2	0.78	4870
27	31	6.1	0.88	5250

[illegible] was [illegible] [illegible] third [illegible] treated water showed re[illegible] fluorides close to the permissible limit (Table 32). The results show that the mixing in baffles basins is better compared to the operation of the plant without the use of paddles. Proper placement of baffles to ensure adequate mixing between test water and reactants may avoid mechanical stirring devices.

TABLE 32

PERFORMANCE OF THE PLANT WITH THE BAFFLES BASIN IN OPERATIONS AND WIHOUT THE PADDLES

Test water fluorides 3.5 to 4.5 mg F/l ; alkalinity 250 to 350 mg $CaCO_3$ /l.

Time, hrs	Alum dose, mg Al/l	pH of the treated water	Fluorides in treated water, mg F/l	Quantity of treated water, litres
3	45	6.3	1.30	600
5	45	6.6	1.50	856
7	50	6.4	1.20	1277
10	50	6.4	1.10	1688
13	38	6.6	0.80	2125
17	33	6.4	0.80	2769
20	40	7.0	0.94	3393
22	42	6.9	0.88	3717
24	37	6.7	0.78	4129
27	36	6.9	1.30	4655
30	45	6.5	1.20	5101

Cost Analysis

The economics aspect of Nalgonda Technique has been analysed for (a) running costs and (b) total operational costs. While under running costs, the expenditure on chemicals alone is included the total operational costs cover depreciation, interest on the capital, personnel, power, maintenance and other running costs. For house-hold treatment, there is no capital investment as such since only a

(a) Running Costs

The optimum requirement of alum (mg Al/l) for different levels of fluorides and alkalinity is shown in Table 26. The dose of filter alum (D) is obtained by multiplying these values by a factor of 13. If sodium aluminate is used, its dose would be (D/100) mg/l. When lime is used instead of sodium aluminate, the corresponding dose is (D/20) mg/l. The cost of sodium aluminate, lime and filter alum* were Rs. 2,000/-, Rs. 200/- and Rs. 700/- per ton (1,000 kg) respectively. Since sodium aluminate is costlier than lime, the running costs are based on the use of lime. Table 33 shows the cost aspects of treatment per m^3 of water as well as per capita annual cost at the rate of 25 l/(capita)(day) consumption for house-hold treatment.

(b) Total Operational Costs

The calculations are based on a typical plant capable of producing 0.5 mgd (2,270 m^3/d) defluoridated water. The plant comprises (FIG. 4) lime feeders, alum tanks, chemical house, mechanical flocculator (30 min), sedimentation basins (4 hrs), rapid gravity sand filter (4.8 m/h or 16 ft/h), chlorination equipment and an overhead storage tank of 450 m^3 (approximately 1,00,000 gallons) capacity. The optimum alum dose required to to produce a treated water with 1.0 $\pm$ 0.3 mg F/l is 'c' mg filter alum per l from a raw water containing 'a' mg F/l and 'b' mg alkalinity/l. The alkalinity in the treated water should not be less than 50 mg/l, as $CaCO_3$ i.e, (b-50) should always be greater than 0.5 'c' numerically. The dose of lime is c/20 mg/l.

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* 1977-78 rates.

[illegible]

[illegible] plant was operated adding fluorides to raw water. The dosing of chemicals was regulated by chemical dosing pump; sodium fluoride and sodium bi-carbonate were dosed to the raw water and fluoride removal studied for about a fortnight. The operation was highly satisfactory and the fluorides were reduced from 2.8-7.1 mg/l to permissive level.

BASIS FOR CALCULATION

(a) [illegible] works

[illegible] works		.. Rs.	3,60,000
[illegible] and [illegible]		.. Rs.	1,20,000
Land		.. Rs.	20,000
	Total	.. Rs.	5,00,000

(b) Depreciation

Civil works @ [illegible] % per annum		.. Rs.	12,[illegible]
Machinery @ [illegible] % per annum		.. Rs.	8,[illegible]
	Total	.. Rs.	20,000

(c) Interest on the Capital @ 10 % on the capital [illegible] .. Rs. 50,000

(d) Personnel

Engineer	..	.. Rs.	12,000
Chemist	..	.. Rs.	9,000
Auxiliary	..	.. Rs.	21,000
	Total	.. Rs.	42,000

(e) Maintenance

Civil works @ 2 % per annum	.. Rs. 7,200	
Machinery @ 5 % per annum	.. Rs. 6,000	13,200

(f) Operational costs

Depreciation		..Rs. 20,000
Interest on capital		..Rs. 50,000
Personnel		..Rs. 42,000
Maintenance		..Rs. 13,200
	Total	..Rs.1,25,200
Add contingencies 5 %		..Rs. 6,260
	Total	..Rs.1,31,460
	or	..Rs. 360 per day

(g) Running Cost (chemicals)

Alum consumption per day	.. 2.27 c kg
Lime consumption per day	.. 0.1135 c kg
Cost of alum @ Re. 0.70/kg Rs.	.. 1.589 c
Cost of lime @ Re. 0.20/kg Rs.	.. 0.023 c
Total cost of chemical treatment per day Rs.	.. 1.612 c

(h) Running Costs (power)

Pumping 20 M head, 60 % efficiency		.. 10 H.P.
Chemical house, flocculator and settling basin		.. 3 ,,
Filter house		.. 2 ,,
Lighting etc.		.. 1 ,,
Miscellaneous		.. 1 ,,
	Total	.. 17 H.P. or 310 units/day
Cost of power per day @ 0.20	Rs...	62/-

(i) Total Operational Costs/day

= Rs. (360.00 + power + chemicals)

= Rs. (360.00 + 62.00 + 1.612 c)

= Rs. (422.00 + 1.612 c)

(j) Operational Costs/m^3 Water Treated

= Rs. (422.00 + 1.612 c)/2270

= Rs. (0.186 + 0.00071 c) where c = mg/l filter alum dose

(k) The cost of treatment per m^3 is therefore a fraction of alum applied and Table 34 summarises the cost at various alkalinity and fluoride levels.

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TABLE [illegible]

RUNNING COST OF DEFLUORIDATION OF WATER AT VARIOUS FLUORIDE AND ALKALINITY LEVELS

Cost of alum - Rs. 700/- per ton: and cost of lime Rs.200/- per ton

Raw water alkalinity, mg $CaCO_3$ /l	Raw water fluorides, mg F/ l: 2	3	4	5	6	8	10	Cost/capita (annum) @ 35 lpcd consumption Rs.**
	(Rs. per m^3 to obtain permissible fluorides in treated water)							
200	0.135	[illegible]	[illegible]	*	*	*	*	[illegible]
310	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	*	[illegible]	[illegible]
400	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.515	*	2.[illegible] - [illegible]
[illegible]	0.249	[illegible]	[illegible]	[illegible]	[illegible]554	0.691	*	2.2[illegible] - [illegible].30
[illegible]	0.286	0.369	[illegible]	[illegible].508	[illegible].66[illegible]	0.794	*	2.6[illegible] - [illegible].24
[illegible]	0.342	0.415	0.469	0.628	0.75[illegible]	0.923	[illegible].071	3.12 - [illegible]
1[illegible]	0.369	0.545	0.565	0.722	[illegible].158	1.015	[illegible].201	3.[illegible] - [illegible]

* Not possible to obtain permissible limit of 1 mg F/l at test water alkalinity.

** Depends on fluoride concentration.

TABLE 34

TOTAL OPERATIONAL COSTS OF DEFLUORIDATION OF WATER AT VARIOUS FLUORIDE AND ALKALINITY LEVELS

(Includes capital, depreciation, interest, personnel, maintenance, chemicals and power)

Cost of alum - Rs. 700/- per ton, Cost of lime Rs. 200/- per ton

Raw water alkalinity, mg $CaCO_3$ /l	Raw water fluorides, mg F per l							Cost /capita (annum) @ 25 lpcd consumption Rs.**
	2	3	4	5	6	8	10	
	(Rs. per m^3 to obtain permissible fluoride in treated water)							
200	0.343	0.393	0.472	0.463	*	*	*	3.13 - 4.23
310	0.380	0.435	0.489	0.546	0.620	*	*	3.47 - 5.67
400	0.408	0.472	0.518	0.611	0.694	0.702	*	3.73 - 6.42
510	0.435	0.546	0.583	0.675	0.740	0.887	*	3.98 - 8.02
600	0.472	0.555	0.611	0.694	0.848	0.980	*	4.30 - 8.96
820	0.520	[illegible]	0.675	0.814	0.943	1.109	1.257	4.83 - 11.50
1070	0.555	0.731	0.851	0.903	1.044	1.201	1.386	5.07 - 12.68

* Not possible to obtain permissible limit of 1 mg F/l at test water alkalinity.

** Depends on fluoride concentration.

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TABLE 35

NALGONDA TECHNIQUE FOR DEFLUORIDATION

Cost of Treatment Vs Pumping Distance of 1 m^3 of water

Raw water, mg F/l	Raw water alkalinity expressed as mg $CaCO_3$ per litre: 200				310			
	Alum dose, mg/l	Cost Rs.	4.8 P * kms.	2.8 P** kms.	Alum dose, mg/l	Cost Rs.	4.8 P* kms.	2.8 P** kms.
2	221	0.343	7.15	12.25	273	0.382	7.96	13.64
3	299	0.398	8.30	14.20	351	0.435	9.06	15.53
4	403	0.472	9.83	16.86	416	0.481	10.02	17.17
5					507	0.546	11.38	19.50
6					611	0.620	12.95	22.14

Raw water, mg F/l	Raw water alkalinity expressed as mg $CaCO_3$ per litre: 400				510			
	Alum dose, mg/l	Cost Rs.	4.8P* kms	2.8P** kms.	Alum dose, mg/l	Cost Rs.	4.8P* kms.	2.8P** kms.
2	312	0.408	8.50	14.57	351	0.435	9.06	15.53
3	403	0.472	9.83	16.86	507	0.546	11.58	19.50
4	468	0.519	10.81	18.53	569	0.583	12.14	20.82
5	598	0.611	12.72	21.82	689	0.675	14.06	24.10
6	715	0.694	14.46	24.43	780	0.740	15.42	26.43
8					988	8.887	18.48	31.68

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Contd.. TABLE 35

Raw water, mg F/l.	Raw water alkalinity expressed as mg $CaCO_3$ per litre: 600 — Alum dose, mg/l	600 — Cost Rs.	600 — 4.8P* kms.	600 — 2.8P** kms.	820 — Alum dose, mg/l	820 — Cost Rs.	820 — 4.8P* kms.	820 — 2.8P** kms.
2	403	0.472	9.83	16.86	468	0.519	10.81	18.53
3	520	0.555	11.56	19.82	585	0.601	12.52	21.46
4	598	0.611	12.73	21.82	689	0.675	14.06	24.10
5	715	0.694	14.46	24.43	884	0.814	17.00	29.07
6	936	0.851	17.73	30.40	1066	0.942	19.62	33.64
8	1118	0.980	20.41	35.00	1300	1.109	23.10	39.60
					1508	1.256	26.17	44.86

Raw water, mg F/l	Raw water alkalinity expressed as mg $CaCO_3$ per litre: 1070 — Alum, dose, mg/l	1070 — Cost Rs.	1070 — 4.8P* kms.	1070 — 2.8P** kms.
2	520	0.555	11.56	19.82
3	767	0.731	16.23	26.10
4	936	0.851	17.73	30.40
5	1010	0.903	18.81	32.25
6	1209	1.044	21.75	37.28
8	1430	1.201	25.02	42.90
10	1690	1.3[illegible]6	28.87	49.50

* 4.8 p are expenses for pumping 1 m^3 water one km using 6" dia C.I. main.
** 2.8 p are expenses for pumping 1 m^3 water one km using 8" dia C.I. main.

Defluoridation recommended, if a raw water source without fluoride is not available within a distance indicated in this column.

[illegible] transportation of [illegible] without [illegible] [illegible] a distance Vs cost of [illegible]luoridation using 'Nalgonda Technique'. When [illegible] use Nalgonda Technique ?

In order to choose between two water sources, one with excess of fluoride and the other with fluoride within the permissible limit, the factor that will govern will be the comparison between cost of defluoridation in first case and transport charges in other case. Hence, the cost to carry 2,270 m^3/d (0.5 mgd) water from a distance was compared with that of defluoridation. Table 35 gives the maximum distance upto which the water having marginal fluoride content can be brought without incurring charges more than defluoridation. The calculations are based on transport charges for carrying water over a length of one k.m. without taking into consideration any static head and using 6" and 8" dia cast iron pipes. The calculations are on the basis of information in Table 36.

TABLE 36

EXPENSES FOR PUMPING 1 m^3 WATER PER 1 K.M.

			Diameter of rising main (C=100)	
			6" dia	8" dia
Head losses due to wall friction along straight uniform 1,000 m length pipes and due to fittings, meters.		..	30	5
Static head (assumed to be zero)		..	0	0
Power requirements, kw.		..	15	2.5
Power requirement per day, kwh		..	360	60
A- power charges per day Rs.		..	72	12
B- cost per 1,000 m CI pipe line	Rs.	..	1,00,000	1,40,000
C- interest on the capital 10%	Rs.	..	10,000	14,000
D- depreciation on the CI pipe line 2.5 % per annum.	Rs.	..	2,500	3,500
E- maintenance 1% per annum on B	Rs.	..	1,000	1,400
F- total expenditure (C + D + E)	Rs.	..	13,500	18,900
G- expenditure per day Rs.		..	37.00	51.78
H- total expenses per day (A+G)	Rs.	..	109.00	63.78
I- expenses for pumping 1 m^3 1,000 m*		..	4.8 paise	4.8 paise

* This does not include cost of (i) treatment, if the source of water is a surface one; (ii) capitalization of pumphouse and (iii) man-power.

From the information presented in this paper, the cost of defluoridation of 1 m^3 water containing 4.3 mg F/l and 216 mg/l alkalinity are given below in Table 37.

TABLE 37

COST OF DEFLUORIDATION OF 1 m^3 OF WATER BY VARIOUS METHODS

Method		Cost Rs. per m^3
Magnesia	..	1.33
Carbion	..	0.60
Serpentine	..	13.00
Defluoron-2	..	0.53
Nalgonda Technique of Defluoridation for Community Treatment	..	0.47
Nalgonda Technique of Defluoridation for Domestic Treatment	..	0.32

Fluoride Estimation

The methods used for the determination of fluoride by various workers at NEERI were as follows :

Defluoridation Method.	Fluoride Estimation Method.
Ion Exchange Resins	Eriochrome cyanine-R; photomestric (64)
Saw dust carbon	-do-
Defluoron-1	-do-
Carbion	-do-
Defluoron-2	Eriochrome cyanine-R & photometric (64) Alizarin Red; photometric (65) SPADNS; photometric (65) Ion Electrode method (65)
Magnesia Serpentine	Alizarin Red; photometric (65) SPADNS; photometric (65) Ion Electrode Method (65)
Nalgonda Technique	-do-

Dixit and Dabadghao (67) have studied the limitations of Eriochrome Cyanine-R Method and observed that aluminium interference does not increase continuously with increase in aluminium ion concentration. Nawlakhe (68) has compared the methods of Eriochrome Cyanine-R, Alizarin Red and SPADNS for fluoride in defluoridated waters. The determinations have been made on both the direct and distilled samples. Steam distillation procedure of the sample has been followed using prechloric acid. The ECR gave lower results while Alizarin Red Method gave higher values. SPADNS Dye Method gave reproducible results. The work at the Institute indicated that the values obtained with SPADNS Dye Method are in good agreement with Ion Electrode Method (66), which gave total fluoride ion concentration (Table 38).

Current Status of Defluoridation

A comprehensive plan for the defluoridation in areas of endemic fluorosis should be investigated and developed. Although several areas are known to be affected by endemic fluorosis, defluoridation has not received due attention. This was primarily due to the non-availability of suitable defluoridation techniques, necessity to handle acids and alkalies for regeneration, unavoidable skilled supervision and high costs of operation. Now that a comparatively cheap process is available, most of the aforesaid constraints are greatly overcome and a beginning can be made to solve the fluorosis problem. It is fortunate that some state governments are now coming forward to utilise the knowledge.

[illegible] DETERMINATION [illegible]
[illegible] AND ION ELECTRODE [illegible]
COMPARATIVE VALUE[illegible]*

S.No.	SPADNS METHOD, mg F/1	ELECTRODE METHOD, mg F/1	DIFFERENCE, mg F/1
1	4.4	4.3	0.1
2	0.09	0.062	0.028
3	0.14	0.071	0.69
4	0.20	0.098	0.102
5	0.35	0.26	0.09
6	0.33	0.23	0.1
7	0.59	0.50	0.09
8	1.15	1.15	0.0
9	1.68	1.50	0.18
10	4.75	4.60	0.15
11	0.46	0.34	0.12
12	0.33	0.26	0.07
13	0.40	0.30	0.10
14	0.53	0.44	0.09
15	0.70	0.70	0.0
16	1.0	1.0	0.0
17	1.24	1.30	0.06
18	1.76	1.60	0.16
19	4.7	4.6	0.1
20	0.86	0.78	0.08
21	0.38	0.25	0.13
22	0.24	0.17	0.07
23	0.24	0.21	0.03
24	0.38	0.26	0.12
25	0.50	0.45	0.05
26	0.90	0.83	0.07
27	1.28	1.20	0.08
28	0.84	0.91	0.07
29	1.36	1.35	0.01
30	4.7	4.5	0.20
31	1.84	1.4	0.44

* Ionalyzer, Specific Ion Meter, Model 407 : Orion Research Inc., 11, Black Stone Street, Cambridge, Massachusetts 02139, USA.

	SPADNS METHOD, mg F/1	ELECTRODE METHOD, mg F/1	DIFFERENCE, mg F/1
32	0.66	0.49	0.17
33	0.44	0.24	0.20
34	0.47	0.23	0.24
35	0.51	0.30	0.21
36	0.63	0.45	0.18
37	0.58	0.42	0.16
38	0.74	0.59	0.15
39	0.89	0.85	0.04
40	1.1	1.25	0.15
41	1.48	1.35	0.13
42	1.20	1.05	0.15
43	1.48	1.30	0.18
44	1.84	1.70	0.14
45	1.84	1.70	0.14
46	1.74	1.55	0.19
47	2.00	1.95	0.05
48	3.20	2.50	0.70
49	3.40	2.85	0.55
50	3.85	3.15	0.70
51	2.85	2.25	0.60
52	3.30	2.80	0.50
53	4.00	3.20	0.80
54	3.00	3.00	0.0
55	3.00	3.00	0.0
56	3.55	3.50	0.05
57	3.85	3.90	0.05
58	4.15	4.20	0.05
59	4.15	4.40	0.25
60	5.25	5.20	0.05
61	0.96	0.98	0.02
62	0.70	0.70	0.0
63	0.63	0.68	0.05
64	1.06	1.15	0.09
65	1.54	1.50	0.04

TABLE 38 .. Contd.

S.No.	SPADNS METHOD, mg F/1	ELECTRODE METHOD, mg F/1	DIFFERENCE, mg F/1
66	2.10	1.95	0.15
67	2.75	2.50	0.25
68	2.75	2.60	0.15
69	3.35	3.10	0.25
70	2.75	2.70	0.05
71	3.25	3.15	0.10
72	3.55	3.75	0.20
73	4.15	4.20	0.05
74	4.25	4.40	0.15
75	4.65	4.80	0.15
76	4.00	4.00	0.0
77	4.45	4.50	0.05
78	5.0	5.0	0.0
79	5.25	5.20	0.05
80	5.30	5.30	0.0
81	2.30	2.45	0.15
82	2.65	2.80	0.15
83	3.35	3.30	0.05
84	3.55	3.55	0.0
85	4.00	4.00	0.0
86	3.95	4.00	0.05
87	4.60	4.40	0.20
88	4.85	4.70	0.15

Scope for further investigations

The removal of excess fluorides from community water supplies to prevent dental disfigurement, loss of teeth and cost of dental care is a sound public health procedure and should be adopted as fast as the community can absorb it. The pre-requisite for this is a comprehensive plan for the defluoridation in all areas of endemic fluorosis which should be investigated and indeed developed. Concurrently with these broad aims, the following programme should be considered for implementation.

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1. A consolidated information on the fluoride levels in underground water and the incidence of fluorosis is not available. Whatever data is available already should be compiled and systematic surveys will have to be initiated where such data is not already available.
2. Detailed maps showing the levels of fluoride at district, state and national level are to be prepared for delineating the problem zones.
3. State governments should be persuaded to take up the issue of defluoridation as the local bodies are under their control. NEERI will provide the necessary technical know-how.
4. A follow-up action is necessary to study the benefits of defluoridation. Steps can be taken to evaluate at periodic intervals in general improvement in the dental health of the consumers of defluoridated water.
5. A perusal of the literature available from different fluoride bearing regions indicates close relationship between the fluoride and the total alkalinity. Fluoride bearing waters are generally high in alkalinity. The incidence of skeletal fluorosis was reported to be higher in soft water areas than in hard water zones, fluoride concentration remaining the same. A study of the chemical data available in these cases indicates the presence of high alkalinity in such waters. There is, therefore, a necessity to find out whether there exists a true correlation between the alkalinity and incidence of fluorosis in such zones.
6. Establishment of ' Fluorosis Index ' for conditions prevailing in India is necessary.
7. While there is sufficient data on fluoride in water, there is practically no information available on fluoride content of food material. A need therefore exists to analyse food material all over India for fluoride content.

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SUMMARY

Fluorine, the most electro-negative of all elements has notable chemical and physiological properties of great interest and importance for human well being. The chemical properties of fluorine, its occurrence in nature and solubility data of fluorine compounds of interest are presented.

The fluoride metabolism, excretion and the effect of fluoride ingestion in human system are briefly reviewed. The effect on dental enamel and deans' classification of mottled enamel into seven categories, ranging from Normal to Severe, are presented. The importance of community index or fluorosis index which defines the degree of severity of mottled enamel is stressed.

Occurrence of fluoride in waters was reported from several states in India and the general level of fluoride is from 1 to 5 mg/l except in a few cases where the concentrations are reported to be as high as 16 mg/l. Several methods have been suggested from time to time for removing excessive fluorides which may be divided into two basic types - those based upon an exchange process or adsorption and those based upon the addition of chemicals to water during treatment. The methods used successfully in other countries which are not readily applicable under Indian condition are briefly reviewed.

The work on defluoridation at NEERI is discussed in details. The various materials studied include clays, ion exchange resins, activated carbons, sulphonated coals, magnesium compounds, serpentine, iron and aluminium salts. Only these that showed an encouraging trend on bench scale are studied in details, are presented in this paper. These include cation and anion exchange resins, saw dust carbon, carbion, defluoron-1, magnesia, serpentine and defluoron-2. Ion exchange resin, saw dust carbon, defluoron-1, magnesia and serpentine have not been found useful beyond bench scale.

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The capacity of various defluoridating media, problems in operation and limitations in their application are brought out. Continuous operation of the large scale defluoridation plants using defluoron-2 resulted in the formation of white deposits over the medium and a consequent fall in the defluoridating capacity by about 60 %. The operating capacity was greatly restored by the acid wash.

Though defluoron-2 process is successful in removing fluorides, the regeneration and maintenance of the plant requires skilled operation which is not always forthcoming. In order to over-come this problem, a new method referred to as ' Nalgonda Technique ' of the defluoridation has been developed and demonstrated. The method is simple and can be adapted even by villagers. The cost of defluoridation has also been brought down considerably. With domestic treatment, capital investment is not necessary and the cost of treatment is only that of the chemicals. At the rate of Rs. 700/- per tonne of alum, 10 lpcd water consumption, 400 mg/l alkalinity and 3-6 mg F/l, the per capita annual cost of treatment works out as between Rs. 1.69 and Rs. 2.23. The cost of defluoridation by Nalgonda Technique was compared with the costs of pumping water.

Different methods of fluoride estimation were used by various workers while studying the problem of defluoridation. The methods adapted with various defluoridation techniques are given.

Scope for further investigations in the area are proposed.

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