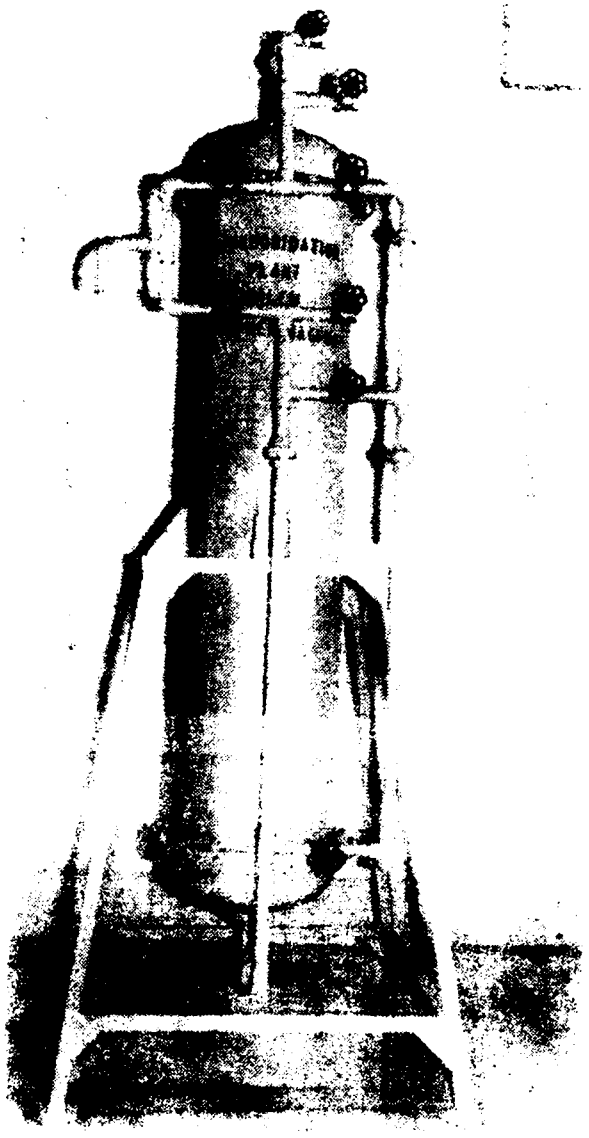


defluoridation

Mottled enamel due to excessive fluorides in water

DEFLUORIDATION

(REVISED)

CENTRAL PUBLIC HEALTH ENGINEERING RESEARCH INSTITUTE
NEHRU MARG, NAGPUR-440020, INDIA

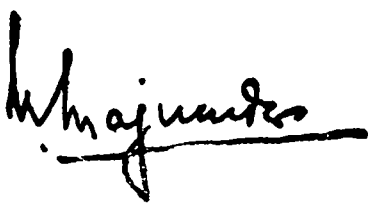
DECEMBER 1973

FOREWORD

A medium "DEFLUORON-2" has been developed for removal of fluorides from water and does not suffer from the handicaps which some of the indigenous media developed earlier suffered from. Laboratory tests have been duly supplemented with pilot plant operations. Cost of defluoridation, using this new medium, ranges from Re. 0.25 to Rs. 1.11 per M^3 depending on fluoride concentration and alkalinity in the raw water. This is mainly due to cost of regeneration with alum. It is hoped that advantage will be taken of this to ameliorate the conditions of thousands of people who are today exposed to "fluorosis" in India.

First edition of this brochure was brought out in June, 1969. In preparing this revised edition the main structure of the brochure has not been altered, but a number of minor changes and additions have been made to bring the information up-to-date on the basis of further experience with Defluoron-2. The cost analysis presented is based on the current market rates in India.

I wish to acknowledge my thanks to S/Shri K. R. Bulusu, B. N. Pathak, V. P. Thergaonkar, D. N. Kulkarni and W. G. Nawlakhe of Water Chemistry Division who worked tirelessly to develop the medium and evaluate its performance characteristics.



(Prof. N. MAJUMDER)
DIRECTOR

Nagpur :
December 1973

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Defluoridation

Defluoridation is a process for reducing the concentration of fluorides present in drinking water and consequently the incidence of fluorosis.

FLUOROSIS

Fluorine is one of those remarkable elements which has not only notable chemical qualities but also physiological properties of great interest and importance for human health. Absence of this element in human diet is known to lead to 'dental caries'. When it is present to the extent of more than 1.2 mg/l in drinking water, it can lead to another disease 'fluorosis'.

A few years after fluorosis was reported in USA, Dr. T. Lakshminarayana, District Health Officer in Nellore, A.P., (India) observed in 1936 the prevalence of a condition similar to fluorosis. Subsequently fluorosis has been reported from several areas in India, particularly Andhra Pradesh, Tamil Nadu, Kerala, Punjab, Haryana and Rajasthan.

It is shown that the severity of fluorosis was directly related to the fluoride concentration in the water consumed during the period of permanent tooth calcification. Children continuously drinking water containing about 5 mg/l or more fluoride are invariably affected with mottled enamel of the permanent teeth; many of these children have gross calcification defects which weaken the enamel and cause eventual loss of teeth through attrition. Other expected effects from excessively high intake levels are*—(a) bone changes when water containing 8-20 mg fluoride per litre is consumed over a long period of time; (b) crippling fluorosis when water with 20 or more mg of fluoride from all sources is consumed per day for 20 or more years, and (c) death when 2250-4500 mg is consumed in a single dose.

OPTIMUM CONCENTRATION OF FLUORIDES

The optimum concentration of fluoride, when no ill effects result, seems to vary with proportion of body weight to the total amount of fluoride consumed from water and food, and with the ambient tempera-

* Shaw, J., Editor. "Fluoridation as a Public Health Measure". A.A.A.S. Pub. No. 38. Washington DC, 1954.

ture. In India, the optimum fluoride concentration in water might vary between 0.5 and 1.2 mg/l depending upon climatic conditions prevalent in different parts of the country. The relationship between fluoride content of drinking water and dental fluorosis is shown in Fig. 1 (after Hodge, 1950).

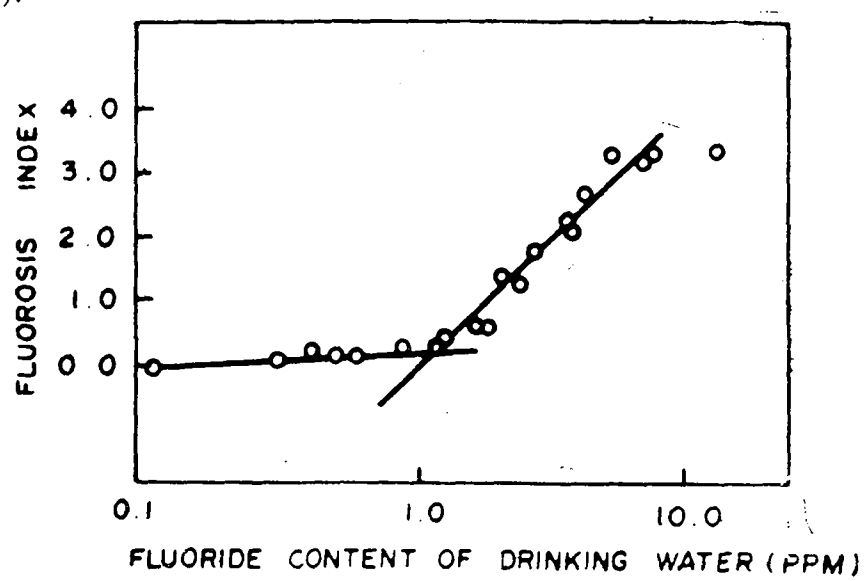

Fig. 1—Relationship between Fluoride Content of Drinking Water and Dental Fluorosis
(HODGE, H. C. [1950] J. Amer. Dent. Assoc., **40**, 436)

DESCRIPTION OF THE PROCESS

In practice, the PHERI Defluoridation Process in its simplest form consists of passing the raw water through a bed of "DEFLUORON-2" medium contained in a cylindrical steel shell to which are attached the necessary pipe work and control valves. Immediately adjacent to the shell the regeneration tank is located so that the whole installation is compact and easily maintained. Fig. 2 is a line diagram of a Defluoridation Plant.

"DEFLUORON-2"

"DEFLUORON-2" is a sulphonated medium developed from indigenous material. It is operated on the aluminium cycle with alum solution as regenerant.

MEDIUM CHARACTERISTICS

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

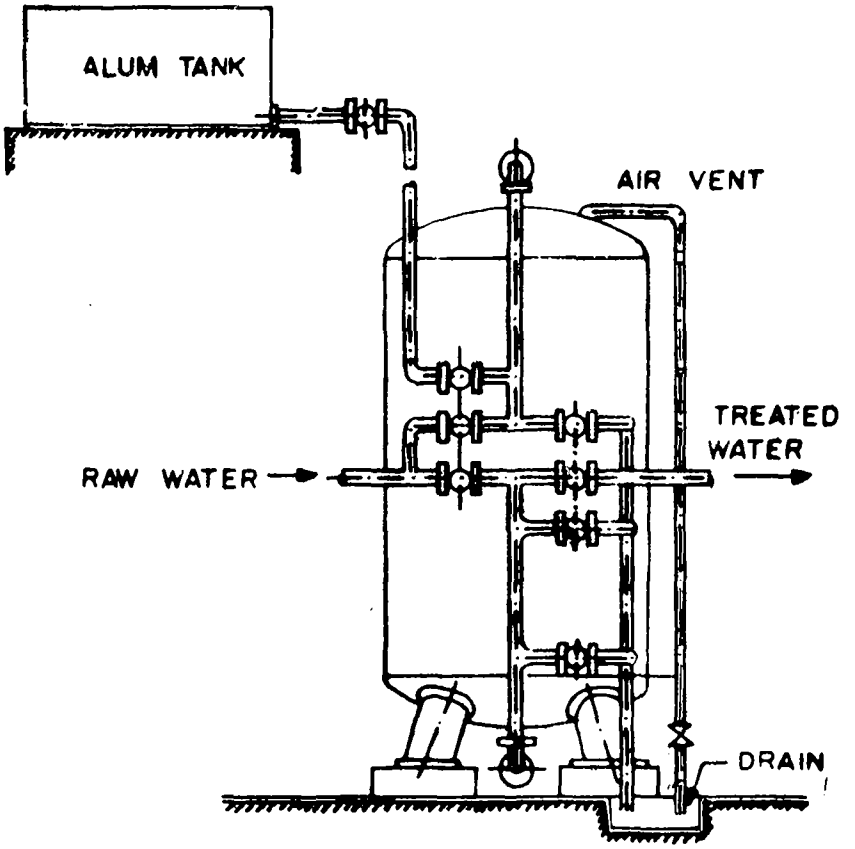

Fig. 2—Defluoridation Plant

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 percent (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.

Pressure drop through the medium

1.2-1.5 meter per meter depth of medium at 5 M^3 per sq. meter bed area per hour flow rate.

Alkalinity tolerance

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 fluorides. These capacities correspond to a raw water alkalinity of 160 mg/l as $CaCO_3$. The capacity of the medium at other alkalinity levels is given below:—

FLUORIDE REMOVAL CAPACITY,* mg FLUORIDE PER LITRE OF MEDIUM

Bicarbonate alkalinity of the raw water mg $CaCO_3$/l	Raw water fluorides, mg per litre			
	3-5	5-7	7-8	8-10
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 percent reduction in the capacity of the medium when hydroxyl alkalinity is 25 mg/l as $CaCO_3$.

The decrease in the capacity of the medium with increase in bicarbonate alkalinity is shown in Fig. 3.

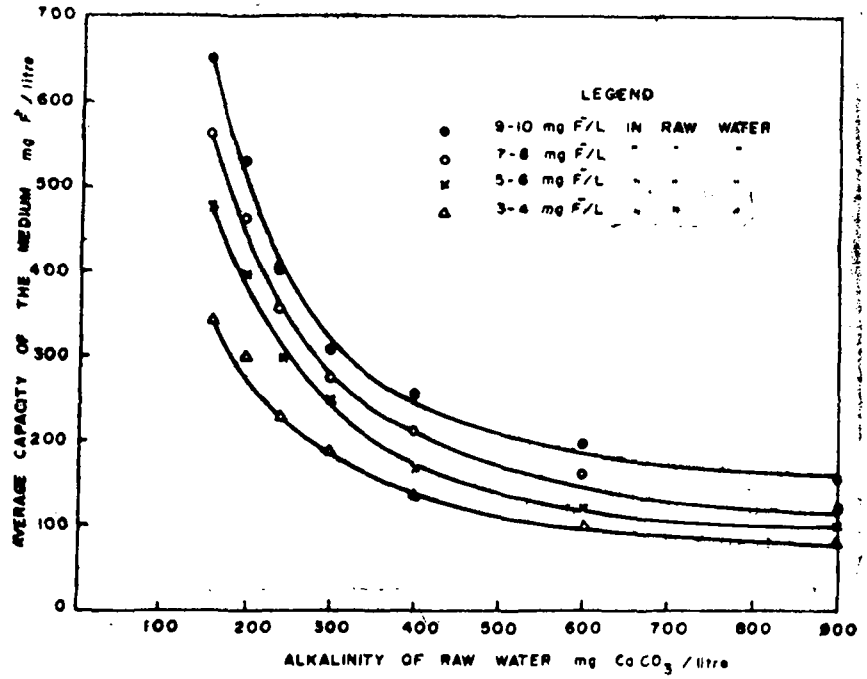

Fig. 3—Reduction in the Capacity of the Medium with Bicarbonate Alkalinity

EXHAUSTION CURVE

An important operating characteristic of "DEFLUORON-2" is given by what is known as an exhaustion curve, a typical example of which is shown in Fig. 4. It shows the way in which the residual fluoride in water

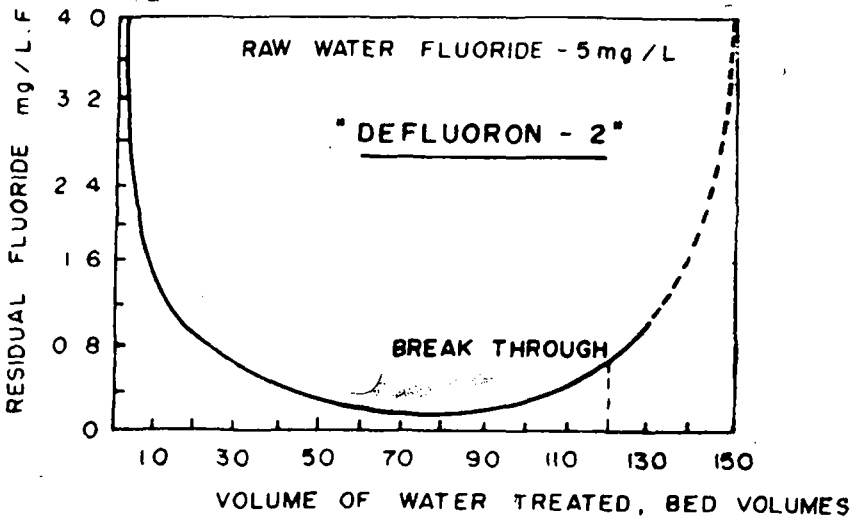

Fig. 4—Typical Exhaustion Curve for "Defluoron-2"

changes with the volume of the water treated. There is a sharp break-through point, after which, with a further quantity of water treated, the fluoride leakage rises steeply. This enables the end of the exhaustion stage of the process to be easily observed. In practice, defluoridation would be stopped well before sharp break-through when a certain concentration of fluoride ion (say 1.2 mg/l) appears in the effluent.

FLUORIDE LEAKAGE TEST

An easy colorimetric test can be used to detect fluorides in water. The test is based on the reaction between fluoride and zirconium-dye lake. The fluoride reacts with the dye lake, dissociating a portion of it into a colourless complex anion (ZrF_6^{--}) and the dle. As the amount of fluoride is increased, the colour produced becomes progressively lighter. Alizarin Red S visual method is suggested as a satisfactory procedure for fluoride evaluation in treated water. Samples collected an hour after the start of the plant can be tested by this method. The details of the test are contained in Annexure B.

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 and the price of alum at site, but as a general rule it may be said that the most of fluoride bearing waters in India contain fluoride ranging from 3 to 10 mg/l and can be defluoridated at a cost between Re. 0.25 and Rs. 1.11 per M^3 (see Table I and Fig. 5). Th e treatment costs increase considerably with alkalinity of the raw water (Table II-V). Annexure A gives cost calculations of CPHERI Defluoridation Plant. The medium requires to be replaced once in every three years.

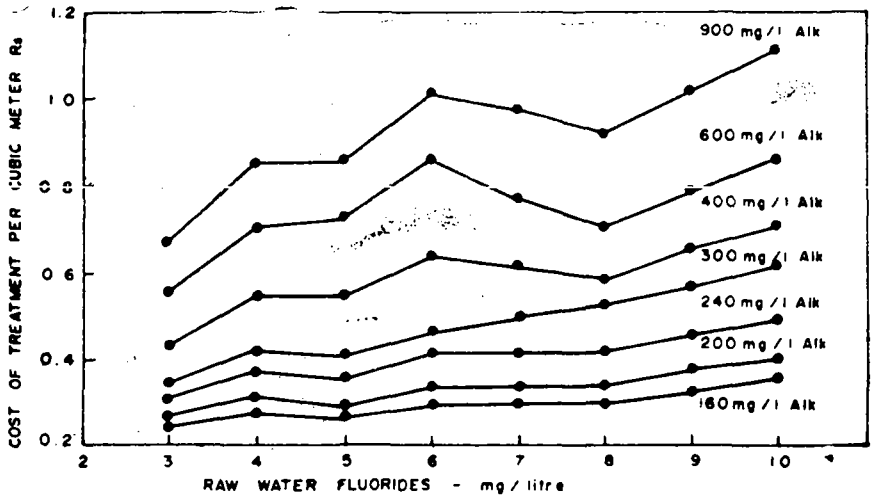

Fig. 5—Cost of Defluoridation at Different Levels of Bicarbonate Alkalinity

TABLE I—RELATIONSHIP BETWEEN RAW WATER FLUORIDE AND COST ESTIMATE*

Fluoride concentration in raw water	Legnth of run between regenerations	Quantity of water treatable per regeneration at maximum rate of 6.8 M^3/hr	Cost of treatment per M^3 (including staff, chemicals, depreciation, power etc.)	Per capita annual cost on the basis of 25 l/capita/day	Capital cost per M^3 of water.
mg/l.	hours.	M^3	Rs.	Rs.	Rs.
3	5.3-22.7	37.33-158.67	0.35-1.11	3.19-10.12	128.51-154.44
4	4.0-17.0	28.00-119.00	0.32-1.01	2.92-9.22	131.17-165.74
5	4.0-19.2	28.00-134.40	0.30-0.91	2.74-8.30	129.96-165.74
6	3.3-16.0	23.33-112.00	0.30-0.98	2.74-8.94	131.84-174.78
7	3.4-16.0	24.00-153.60	0.30-1.01	2.74-9.22	131.84-173.27
8	3.9-16.3	26.75-113.75	0.27-0.86	2.46-7.85	131.66-168.75
9	3.3-14.4	23.33-101.11	0.29-0.86	2.65-7.85	133.06-174.78
10	3.0-13.0	21.00-91.00	0.25-0.67	2.28-6.11	134.44-180.80

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

TABLE II—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 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 25 l/capita/day Rs.
		RAW WATER FLUORIDES-10 mg/l			
160	91.00	150.62	0.35	94	3.19
200	74.28	147.17	0.40	112	3.65
240	56.00	141.47	0.47	143	4.47
300	42.00	134.40	0.61	181	5.57
400	35.00	129.23	0.71	210	6.48
600	28.00	122.18	0.86	248	7.85
900	21.00	112.00	1.11	303	10.13
		RAW WATER FLUORIDES-9 mg/l			
160	101.10	152.19	0.32	95	2.92
200	82.04	149.02	0.37	114	3.38
240	62.22	143.74	0.45	146	4.11
300	46.67	137.14	0.56	185	5.11
400	38.89	132.28	0.65	214	5.93
600	31.11	125.61	0.78	254	7.12
900	23.33	115.86	1.01	313	9.22

TABLE III—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 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 25 l/capita/day Rs.
		RAW WATER FLUORIDES-8 mg/l			
160	113.75	153.80	0.30	96	2.74
200	92.75	150.91	0.34	115	3.10
240	69.99	146.08	0.41	147	3.74
300	52.50	140.00	0.53	189	4.65
400	43.75	135.45	0.59	219	5.38
600	35.00	129.22	0.71	262	6.48
900	26.25	120.00	0.91	324	8.30
		RAW WATER FLUORIDES-7 mg/l			
160	112.00	153.60	0.30	78	2.74
200	92.00	150.79	0.34	93	3.10
240	70.00	146.08	0.41	118	3.74
300	54.00	140.65	0.50	148	4.56
400	42.00	134.40	0.61	181	5.67
600	32.00	126.49	0.77	224	7.03
900	24.00	116.67	0.98	276	8.94

TABLE IV—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 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 25 l/capita/day Rs.
		RAW WATER FLUORIDES-6 mg/l			
160	112.00	153.60	0.30	78	2.73
200	93.33	151.01	0.34	92	3.10
240	70.00	146.08	0.41	118	3.74
300	58.33	142.37	0.47	138	4.29
400	39.67	132.83	0.64	190	5.84
600	28.00	122.18	0.86	247	7.85
900	23.33	115.86	1.01	282	9.22
		RAW WATER FLUORIDES-5 mg/l			
160	134.40	155.52	0.22	66	2.46
200	112.00	153.60	0.30	77	2.73
240	84.00	149.33	0.36	100	3.28
300	70.00	146.08	0.41	118	3.74
400	47.60	137.63	0.55	164	5.02
600	33.60	128.00	0.73	216	6.66
900	28.00	122.18	0.86	247	7.85

TABLE V—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 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 25 l/capita/day Rs.
		RAW WATER FLUORIDES-4 mg/l			
160	119.00	154.38	0.29	73	2.65
200	105.00	152.73	0.32	83	2.82
240	80.50	148.61	0.38	105	3.47
300	66.50	145.09	0.43	124	3.92
400	49.00	138.35	0.55	160	5.02
600	35.00	129.23	0.71	210	6.48
900	28.00	122.18	0.86	247	7.85
		RAW WATER FLUORIDES-3 mg/l			
160	153.67	157.57	0.25	56	2.28
200	140.00	156.28	0.27	64	2.46
240	107.33	153.03	0.31	81	2.83
300	88.67	150.21	0.35	96	3.19
400	65.33	144.73	0.44	126	4.02
600	46.66	137.14	0.56	166	5.11
900	37.33	131.12	0.67	199	6.40

ANNEXURE—A

RELATIONSHIP BETWEEN WATER FLUORIDE AND COST OF TREATMENT

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 and b	...	c „	fluorides per 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. 16,000	
Cost of 1.41 M^3 of medium at the rate of Rs. 1.81 per litre (Rs. 51 per cu ft)	...	Rs. 2,550	Rs. 18,550

II *Depreciation*

Plant at 20 percent per annum	...	Rs. 3,200	
Medium at 33.3 percent per annum	...	Rs. 850	Rs. 4,050

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

Cost = Plant + (medium x 1.67)
= Rs. 16,000 + Rs. 2,550 x 1.67
= Rs. 20,250

C **Sample calculation for a mg/l fluorides and b mg/l alkalnity**

Capacity of the medium = c mg F per litre of material.

Total fluoride removal capacity of the plant between two successive regenerations = 1410 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.

$$\text{Number of actual regenerations/day} = \frac{24\ \text{H}}{(0.2\ c + 1.5\ a)}$$

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

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

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. 0.35 per kg.

$$= \frac{0.35 \times 1344\ a}{(0.2\ c + 1.5\ a)}\ \text{Rupees} \qquad (1)$$

Depreciation per day = Rs. 4050 / 365 = Rs. 11.10 (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 friction losses and @ Re. 0.10 per unit of power)

$$= \frac{1000 \times Q \times 18.28 \times 10}{102 \times 60 \times 60 \times 100} = \frac{0.168\ a}{(0.2c + 1.5\ a)} \qquad (3)$$

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

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

$$= \frac{470.4\ a}{(0.2c + 1.5\ a)} + 11.10 + \frac{0.167\ c}{(0.2\ c + 1.5\ a)} + 8.00$$

$$= 19.10 + \frac{469\ a + 0.167\ c}{(0.2\ c + 1.5\ a)}$$

$$= \frac{(497.65\ a + 3.987\ c)}{(0.2\ c + 1.5\ a)}$$

Cost of treatment per M^3 rupees = K/Q

$$= \frac{497.65\ a + 3.987\ c}{33.6\ c}$$

$$\text{Capital cost per } M^3 \text{ rupees} = \frac{20{,}250}{Q}$$

ANNEXURE—B

ESTIMATION OF FLUORIDE*

(Alizarin Visual Method)

A) **Chemicals :**

1) Standard Fluoride Solution (1.0 ml = 0.01 mg F^-)

Dissolve 0.2210 gms of anhydrous (previously dried in hot air oven at 104°C for an hour) Sodium fluoride (NaF) in distilled water and dilute to one litre. Dilute 10 ml of this to 100 ml. One ml of diluted solution will give 0.01 mg F^-.

2) **Zirconyl-alizarin acid solution**

Dissolve 0.30 gm zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) in (50 ml) distilled water taken in one litre glass stoppered volumetric flask. Dissolve 0.07 gm of 3-alizarin sulfonic acid sodium salt (also called alizarin Red-S) in (50 ml) distilled water. Slowly pour this in zirconyl solution. The solution becomes clear after a few minutes.

Mixed acid:— Dilute (101 ml) conc. HCl to approximately 400 ml. Add 33.3 ml conc. H_2SO_4 to (400 ml) distilled water. Mix the two acids after cooling.

Mixed reagent:— To the clear zirconyl-alizarin reagent in the one litre flask, add the mixed acid solution. Add distilled water upto the mark and mix.

B) **Glassware :** (i) 50 ml Nessler-tubes — one dozen
(ii) 5 „ Graduated pipettes — two numbers.

C) **Procedure:—** In five Nessler tubes prepare fluoride standards by taking 2, 4, 6, 8 and 10 ml of standard fluoride solution. This corresponds to 0.4, 0.8, 1.2, 1.6 and 2.0 mg F^-/litre. Make the volume to 50 mark in all the tubes. In the sixth tube take 50 ml raw water sample.

Add 2.5 ml of the alizarin reagent respectively in all tubes. Mix well and allow the colour to develop for one hour. Compare the colour of tube containing raw water with standard ones.

Fluoride (as mg/l F^-) = 0.4 x Number of tubes with comparable colour

Note:—In case of excess fluoride in raw water, dilute the sample.

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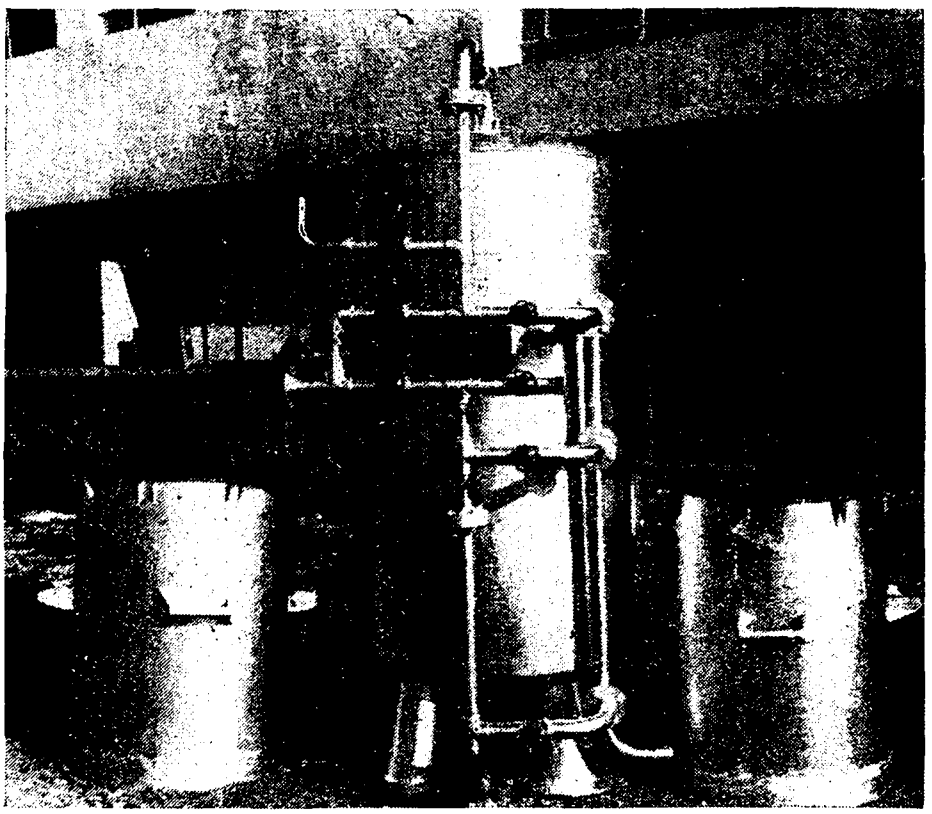
* Based on the Standard Methods for the Examination of Water and Waste Water, *13th Ed. APHA, AWWA, and WPCF, 1971.*



A typical defluoridation plant

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