RE-PRINTS

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Studies on the removal of fluorides from water
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STUDIES ON THE REMOVAL OF FLUORIDES FROM WATER.

Parts I and II.

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Part I.

THE USE OF ION-EXCHANGE RESINS.

THE presence of over one part per million (p.p.m.) of fluorine in drinking water has been found to cause mottling of the enamel of the teeth in children. Concentrations of 3 p.p.m. or over cause irregular outgrowths of osseous tissue on the long bones and ossification of the inter-costal ligaments (Shortt *et al.*, 1937). Cattle lose their condition and develop dragging gait. Exostoses may develop on the ribs and long bones (Shortt *et al.*, 1937a).

The occurrence of fluorides in the drinking waters has been reported from practically all parts of the world. In India, fluorides have been reported to occur in parts of the Madras Presidency (Raghavachari and Venkataramanan, 1940), in Travancore (Pillai, 1938), in Hyderabad (Deccan) (Davar, 1945) and in the Punjab (Wilson, 1939 ; Khan and Wig, 1945). Mottling of the teeth enamel has been noticed in all these areas, while skeletal changes have been observed in some of the endemic areas of the Madras Presidency where the fluorine content of the water varies between 3 p.p.m. and 6 p.p.m.

The various methods which have been suggested from time to time for employment in the removal of fluorides from water may be classified broadly into those : (*i*) involving treatment with chemicals, such as aluminium sulphate (Boruff, 1934 ; Boruff *et al.*, 1937 ; Kempf *et al.*, 1935), lime (Boruff, *loc. cit.*), magnesia (Elvove, 1938) or calcium phosphate which may be added as the powder (McIntire and Hammond, 1938) or precipitated *in situ* (McIntire, 1938), and (*ii*) involving

percolation through beds of contact materials, such as processed bone (Smith and Smith, 1938; Smith and Davey, 1940), activated carbon (McKee and Johnstone, 1934), activated alumina (Churchill, 1937; Fink and Lindsay, 1936), or granular (patented) tricalcium phosphate (Adler *et al.*, 1938; Goodwin and Litton, 1941). Methods in the first group suffer from the disadvantage that they require elaborate treatment plants and careful control over the dose of the chemicals and the pH In some cases, a second treatment may be necessary to restore the pH of the treated water to normal levels. On the other hand, percolation methods do not call for much skill in operation and are hence worthy of study.

Robertson (1939) observed that fluorides are removed from a water containing fluorides when it is percolated successively through beds of phenol-formaldehyde (cation-exchange) and amine-formaldehyde (anion-exchange) resins. Benson *et al.* (1941) reported that fluorides could be reduced from 10 p.p.m. to 1 p.p.m. by successive passage through beds of a cation-exchanger ('Zeokarb H') of the sulphonated coal-type and an amine resin 'Nalcite B'. Better reductions could be obtained by using a second unit of cation- and anion-exchange materials.

In the course of other studies, one of us (K. V.) had developed a cation-exchange resin by condensation of the extract of a local tanning bark (*Cassia auriculata*: vernacular 'Avaram') with formaldehyde. It was considered desirable to study the possibility of using this cation-exchanger in conjunction with different anion-exchangers for the removal of fluorine from water.

EXPERIMENTAL.

Materials.—The cation-exchanger was the tannin-formaldehyde condensation product prepared from 'Avaram' (*Cassia auriculata*) bark. The anion-exchangers studied were: (*a*) Amberlite IR-4 (kindly supplied by the Resinous Products Company, Philadelphia), (*b*) a resin prepared from meta-phenylene-diamine, and (*c*) aniline black deposited on a bed of pumice.

Most of the experiments were conducted with a solution of sodium fluoride (equivalent to 5 p.p.m. of fluorine) in the town water-supply (filtered river-water) whose analysis is given in Table I. A few experiments were run with natural fluorine-bearing waters obtained from the endemic areas.

TABLE I.

Analysis of municipal water-supply used for making solution of sodium fluoride.

		Parts per 100,000.
Total solids	...	17·8
Chlorides as chlorine	...	2·5
Total hardness as CaCO$_3$	...	10·5
Permanent ,, ,, ,,	...	4·2
Temporary ,, ,, ,,	...	6·3
Alkalinity as CaCO$_3$ ...	...	12·0
pH	...	7·4
Fluorine	...	*Nil.*

Preparation of the exchange materials.—The cation-exchanger was prepared by refluxing a sulphited extract of the 'Avaram' bark with formaldehyde and promoting gel-formation with the aid of a small quantity of acid. The air-dried gel was powdered, boiled with acid, washed thoroughly and dried.

The meta-phenylene-diamine-resin was prepared by reacting a solution of freshly distilled meta-phenylene-diamine in hydrochloric acid with formaldehyde to obtain a gel (Kirkpatrick, 1938).

Aniline black (Lange) was deposited on pumice (powdered to pass through a 40-mesh sieve but retained on 60 mesh) as follows: The pumice was soaked overnight in solution I containing 40 g. ferrous sulphate, 40 g. copper sulphate and 90 g. potassium permanganate in 830 c.c. of distilled water. The flask containing the pumice and solution was repeatedly evacuated to enable the solution to fill the pores. The pumice was filtered off and added to solution II containing 120 g. aniline and 180 g. hydrochloric acid in 700 c.c. water. The contents were boiled for 10 minutes, left overnight and then the pumice was filtered off and washed with distilled water. The black powder was boiled with 250 c.c. of deci-normal sodium-hydroxide solution and washed till free of alkali, chlorides and colour.

Activation of the exchange materials.—The cation-exchanger was converted into its hydrogen form by percolation of 10 per cent solution of hydrochloric acid followed by thorough washing with distilled water. The anion-exchangers were similarly treated with 2 per cent solution of sodium carbonate and washed.

The water containing fluorides was percolated at a rate equivalent to 2 gallons per sq. ft. per minute through a bed of 100 g. (315 c.c.) of the acid-treated cation-exchanger (+20, —40 mesh) supported on a layer of glass-wool in a glass-tube of 3·8 cm. internal diameter. Percolation was discontinued when the effluent began to show a perceptible decrease in titrable acidity as compared with the first lot of the percolate. The exhausted resin was regenerated by percolation of 10 per cent hydrochloric acid followed by thorough washing with distilled water.

The pooled mixture of these effluents was then percolated through a similar bed of 20 g. (62 c.c.) of the alkali-treated anion-exchanger in a similar glass-tube. The effluents were collected in lots of 250 c.c. and analysed for their content of total solids, alkalinity, hardness and fluorine. Percolation through the bed was discontinued when the fluorine content of the effluent rose to 1 p.p.m. and the bed was regenerated by percolation of 2 per cent solution of sodium carbonate and washed free with distilled water.

The bed of Amberlite IR-4 was operated repeatedly to study the capacity on successive operation. In one set of experiments the rate of percolation was varied (by using different calibrated nozzles at the outlet) to study whether the capacity is affected by the rate of percolation and whether the resin suffers deleteriously by using an excessive rate of flow. To study the effect of other ions on the capacity of Amberlite IR-4 to take up fluorine, experiments were conducted with solutions of sodium fluoride in different natural waters.

Ion-exchange resins are not capable of removing silica from water. Bauman *et al.* (1947) report that ion-exchange resins can be made to take up silica provided sodium fluoride is added to the water so that the silica is present as H_2SiF_6 when it comes in contact with the anion-exchanger. Conversely, it should be possible

to improve the fluorine-removal capacity of the anion-exchange resin by feeding an influent containing the fluoride as the (SiF_6)-anion. To verify this suggestion, it was decided to compare the fluorine-removal capacity of two identical Amberlite beds—one percolated by a solution containing sodium fluoride alone and the other by a solution containing the same amount of sodium fluoride in addition to sodium silicate. Preliminary experiments were conducted with solutions of sodium fluoride equivalent to 2·2 p.p.m. fluorine in tap-water. To one-half of each of these solutions was added a solution of sodium silicate so that the ratio of SiO_2 (determined by analysis) to fluorine was slightly greater than the stoichiometric equivalent required by (SiF_6)-ion.

Analytical methods.—Total solids, alkalinity and total hardness were estimated by standard methods employed in water analysis, while fluorides were estimated by the colorimetric method using zirconium nitrate and alizarin S (Sanchis, 1934).

RESULTS AND DISCUSSION.

It will be seen from Table II that the ion-exchange system consisting of the 'Avaram'-bark resin and Amberlite IR-4 can remove fluorine efficiently both from an artificially fluorinated water and from natural fluorine-bearing waters. *Meta-phenylene-diamine resin* and *aniline black* are also able to remove fluorides but their capacity is much less than that of Amberlite IR-4. In the case of aniline black, a pink colour is 'thrown' into the treated water but it was found that this colour could be easily removed by percolation through a bed of Jewel granular activated carbon.

TABLE II.

Volume of water treated by 20 g. of the anion-exchanger to 'breakthrough' of 1 p.p.m. of fluorine.

Anion-exchanger.	Artificially fluorinated tap-water. F : 5·0 p.p.m., c.c.	NATURAL FLUORIDE-BEARING WATERS FROM :	
		Podili. F : 2·4 p.p.m., c.c.	Guntakal. F : 1·8 p.p.m., c.c.
Amberlite IR-4	4,250	15,750	15,500
Meta-phenylene-diamine resin ...	1,000	...	...
Aniline black on pumice ...	1,000	...	...

An additional advantage with the ion-exchange unit is that the treated water is completely softened and partly de-mineralized as shown in Table III :—

TABLE III.

Analyses of raw water and water treated by cation-exchanger and Amberlite IR-4.

Water sample.	TAP-WATER WITH FLUORINE.		WATER FROM PODILI.		WATER FROM GUNTAKAL.	
	Raw.	Treated.	Raw.	Treated.	Raw.	Treated.
pH	7·4	6·5	7·6	6·0	7·6	6·0
Total solids, p.p. 100,000 ...	17·8	4·1	51·0	6·3	69·0	10·0
Alkalinity as CaCO₃, p.p. 100,000.	12·0	0·8	30·0	0·9	35·4	0·6
Total hardness, p.p. 100,000 ...	10·5	1·2	23·5	0·9	28·3	0·5
Chlorides as chlorine, p.p. 100,000.	2·5	0·1	6·2	*Nil*	2·3	*Nil.*
Fluorine, p.p.m. ...	5·4	0·5	2·4	0·4	1·8	0·5

Repeated operation with Amberlite IR-4 has shown a slight loss in capacity between the first and second cycle but the capacity has remained at a constant value over the next four cycles of operation as indicated by the results given in Table IV :—

TABLE IV.

Effect of repeated operation through Amberlite IR-4.

(Percolation at approximately 2 gallons per sq. ft./min.)

Number of run :—	I	II	III	IV	V	VI	VII	VIII
Volume in c.c. percolated through 20 g. to 'breakthrough' of 1 p.p.m. of fluorine.	9,000	6,000	5,500	6,000	6,000	5,750	6,000	6,250

Increasing the rate of percolation through the bed of Amberlite IR-4 reduces the quantity of water that could be treated by a given volume of the bed. When, however, the rate was increased beyond the maximum of 5 gallons per sq. ft. per minute prescribed by the manufacturers, the resin did not show any permanent impairment of capacity (Table V) :—

TABLE V.

Effect of increasing the rate of percolation on capacity.

EXPERIMENT I ... {	Rate of flow, gals./sq. ft./min. ...	1·8	1·8	4·2	1·8
	Volume treated in c.c.	8,000	6,000	750	6,000
EXPERIMENT II ... {	Rate of flow, gals./sq. ft./min. ...	1·8	5·4	1·8	1·8
	Volume treated in c.c.	7,500	350	7,000	6,500

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Fluorine is not removed by the cation-exchanger or the anion-exchanger when used alone. To enable the anion-exchanger to take up the fluorine, it is necessary to first pass the water through a hydrogen-ion-exchanger. The efficiency of fluorine removal by the anion-exchanger is largely influenced by the efficiency with which the primary bed of hydrogen-ion-exchanger functions as will be seen from the results given in Table VI, which compares the behaviour of the anion-exchange bed when shaken and fed with the effluents obtained from the cation-exchanger at different stages of exhaustion :—

TABLE VI.

	Lot number of cation effluent.	Acidity p.p. 100,000 CaCO₃.	Final fluorine p.p.m.
(a) 2 g. IR-4 shaken with 200 c.c. of cation-resin effluent. F=5·0 p.p.m.	I II	15·5 4·0	2·2 4·6
(b) Percolation of Guntakal water. F=1·7 p.p.m. through cation resin and then through 20 g. IR-4	I VI	8·5 0·7	0·0 0·1
	Cation bed regenerated. IR-4 not regenerated.		
	I II	8·5 7·5	0·3 0·2
(c) Percolation of tap-water containing sodium fluoride through cation resin and then through 20 g. IR-4 (initial F=5·2 p.p.m.) ...	I IX XII	14·6 8·4 3·0	0·1 2·0 4·0
	Cation bed regenerated. IR-4 not regenerated.		
	I	14·4	0·4

The efficiency of fluorine removal is also influenced by the total salt content of the raw water as will be seen from the results presented in Table VII :—

TABLE VII.

Percolation of cation-exchanger effluent through 20 g. of Amberlite IR-4.

Water used.	PARTICULARS*.						Volume treated in c.c.
	1	2	3	4	5	6	
Sodium fluoride in distilled water.	...	...	...	...	....	2·5	12,000
Sodium fluoride in tap-water ...	21·2	12·0	2·5	2·8	Nil	2·5	6,800
Sodium fluoride in dug-well water.	71·2	26·4	10·7	6·3	2·5	2·5	2,400

*1. Total solids parts per 100,000. 3. Chloride p.p. 100,000. 5. Nitrate p.p. 100,000.
 2. Alkalinity   „   4. Sulphate   „   6. Fluorine p.p.m.

This decrease in efficiency is presumably due to the competition of the other ions with the fluoride-ion for being absorbed on the active groups of the anion-exchanger. This view receives confirmation from an experiment in which two identical beds of Amberlite IR-4 were percolated respectively by (a) a solution of sodium fluoride (in tap-water) which had passed through a bed of cation-exchanger and (b) the same solution of sodium fluoride whose pH was adjusted by the addition of hydrochloric acid to bring it to the same value as that of the cation-exchanger effluent. It will be seen from Table VIII that the fluoride removal is much less in the latter case where the addition of acid has resulted in the enrichment of the anion (chloride) content :—

TABLE VIII.

Effect of increasing the content of anions by the addition of acid.

Influent.	pH.	Acidity as $CaCO_3$.	Total solids.	Chloride.	Volume to ' breakthrough in c.c.
Sodium fluoride in tap-water passed through cation-exchanger.	2·9	6·0	9·6	2·5	4,250
Sodium fluoride in tap-water to which HCl was added.	2·9	9·0	29·8	12·1	200

Preliminary experiments showed that the ability of Amberlite IR-4 to remove fluorides can be improved by the addition of sodium silicate to the raw water (Table IX) :—

TABLE IX.

Effect of addition of sodium silicate to raw water containing fluorides.

	MILLIGRAMMES OF FLUORINE REMOVED BY 20 G. FROM 2,000 C.C. OF CATION-EXCHANGER EFFLUENT.		
	Initial fluorine, p.p.m.	Final fluorine, p.p.m.	Mg. F. removed.
Tap-water containing NaF ...	2·1	1·0	0·3
Tap-water containing NaF and sodium silicate equivalent to 120 p.p.m. SiO_2.	2·1	0·3	3·6

Part II.*

THE USE OF ALUM-TREATED ION-EXCHANGE RESINS.

While cation-exchangers of a satisfactory quality can be prepared from indigenous raw materials, the preparation of anion-exchange resins is difficult because the raw materials—the polyamines—are not available in India. Hence, it was considered necessary to investigate methods which would dispense with the need for the anion-exchange resins.

Metallic aluminium has been suggested (Kramer, 1934) for use in percolation columns but suffers from the disadvantage that appreciable amounts of aluminium-ions find their way into the treated water (Raghavachari *et al.*, *loc. cit.*). One method of overcoming this difficulty would be to employ a second bed of cation-exchanger to trap the aluminium-ions. It would be more preferable to use a material which would contain the ions of aluminium in a reactive but non-leachable form.

Myers and Herr (1945) have taken out a patent for the use of an alum-treated anion-exchange resin for fluorine removal. It was felt that it would be worth while studying if the cation-exchange resin prepared in this Laboratory from the ' Avaram ' (*Cassia auriculata*) bark could be used after treatment with alum.

EXPERIMENTAL.

Preliminary experiments were conducted to compare the relative efficiencies of (*i*) the ' Avaram '-bark resin, (*ii*) the anion-exchange resin Amberlite IR-4, and (*iii*) a proprietary product known as alumina zeolite after they had been treated with a solution of aluminium sulphate. A few experiments were also carried out with the ' Avaram '-bark resin treated with ferric-sulphate solution.

The ' Avaram '-bark resin was first converted into the hydrogen-ion exchange form by percolation of a 10 per cent (v/v) solution of hydrochloric acid, washed free of acidity and then percolated by a solution (1 g. in 100 c.c.) of aluminium sulphate or ferric sulphate, dissolved with the aid of a little acid to prevent hydrolysis. The Amberlite IR-4 was partially converted to the salt form as described by Myers and Herr (*loc. cit.*) before percolation of the solution of aluminium sulphate. The alumina zeolite was thoroughly washed before percolation of the alum solution. In all cases the materials were washed free of aluminium or iron.

Ten g. lots of these materials were supported over a layer of glass-wool in a tube of 0·75″ internal diameter and percolated at a slow rate by a solution (equivalent to 2·5 p.p.m. of fluorine) of sodium fluoride, in the municipal tap-water. Effluents were collected in lots of 200 c.c. and analysed for fluorine by the zirconium-alizarin colorimetric method. Aluminium was estimated in the composite representing 1,000 c.c. by the hæmatoxylin method.

The results of this preliminary study presented above show that the ' Avaram '-bark resin treated with alum is superior to the other materials, both as regards the capacity to remove fluorine and the freedom of the treated water from aluminium. Subsequent experiments were, therefore, confined to this material. Twenty-five g. (67 c.c.) of the resin (passing 20 and retained on 40 mesh) were supported in a glass-tube of 1·0″ diameter and percolated by a solution of sodium fluoride equivalent to 5 p.p.m. of fluorine, the effluents being collected in lots of one litre each.

* Part II is by K. Venkataramanan alone.

TABLE X.

Material percolated.	Fluorine p.p.m. in the influent.	Fluorine p.p.m. in successive lots.					Aluminium or iron in the composite p.p.m.
		I	II	III	IV	V	
'Avaram' resin containing alum	2·5	0·1	0·4	0·5	0·6	1·2	*Nil.*
'Avaram' resin containing iron	2·5	1·7	1·7	2·0	1·8	1·9	0·058
Amberlite IR-4 containing alum	2·5	1·0	1·8	2·0	2·0	2·5	0·278
Alumina zeolite containing alum	2·5	0·6	1·3	1·5	1·8	2·0	0·084

It is known that the colorimetric estimation of fluorine is interfered with by the presence of over 5·0 p.p.m. of aluminium (Walker and Finlay, 1940). Although the concentrations of aluminium in the treated water were much smaller, it was considered desirable to make sure of the reality of fluorine-removal by evaporating an aliquot of the treated water with a fixative (consisting of calcium and m gnesium oxides and magnesium acetate) ashing the residue below 550°C., distilling the ash with sulphuric acid and silica at 135 ± 2°C., and estimating the fluorine in the distillate by the colorimetric method. Two lots (each of 100 c.c.) of the distillate were collected and the completion of the volatilization of fluorine was indicated by the absence of any fluorine in the second lot.

From the results presented in Table XI it will be seen that 25 g. of the resin can deal with 5 to 6 litres of the water containing 5 p.p.m. of fluorine before permitting toxic (1·0 p.p.m.) amounts of fluorine to leak through. Thus, one lb. of the material can deal with approximately 24 gallons of such a water.

TABLE XI.

Experiment number.	Initial.	Number of lots of one litre :					
		I	II	III	IV	V	VI
I. Fluorine p.p.m.	4·2	0·4	0·6	0·5	0·8	1·0	1·2
II. Fluorine p.p.m.	5·0	0·4	0·4	0·6	0·8	1·1	1·2

Besides removing fluorides, this resin was able to reduce the alkalinity, hardness and total solid contents of the water as will be seen from Table XII which gives the analysis of the composite of 6 litres passed through 25 g. of resin :—

TABLE XII.

	EXPERIMENT I :		EXPERIMENT II :	
	Initial.	Final.	Initial.	Final.
Total solids, p.p. 100,000	20·6	7·8	18·6	7·8
Total hardness, p.p. 100,000.	8·0	0·6	8·6	0·8
Alkalinity as CaCO₃, p.p. 100,000.	9·4	0·2	9·5	0·3
Fluorine, p.p.m. ...	4·2	0·8	5·0	0·7

Regeneration.—Percolation of the solution of sodium fluoride was discontinued when the fluorine content of the effluent rose to 1·0 p.p.m. and the bed was percolated by a solution of 1 g. of commercial aluminium sulphate in 100 c.c. of distilled water. The same solution was put back and held in contact overnight after which the bed was drained, washed free of alum and again percolated by the solution of sodium fluoride. Repeated operation over six cycles showed no deterioration in the capacity of the bed for fluorine removal.

An attempt was made to study the possibility of using a solution of sodium carbonate as a regenerant. Two identical beds of 10 g. each were set up and percolated by the same solution of sodium fluoride. They were both regenerated by alum and studied over the second cycle to make sure that their capacities were identical. In subsequent cycles one of the beds was regenerated by alum, while the other was regenerated by 2 per cent sodium carbonate. The beds were washed free of the regenerants and percolated by the solution of sodium fluoride. It may be concluded from the results in Table XIII that sodium carbonate is not useful as a regenerant :—

TABLE XIII.

Treatment.	FLUORINE P.P.M. IN THE		
	Influent.	Effluent bed I.	Effluent bed II.
Both beds regenerated by alum ...	4·6	1·1	1·1
Bed I regenerated by alkali ... Bed II regenerated by alkali ...	5·2	5·2	0·6
Bed I regenerated by alum ... Bed II regenerated by alkali ...	5·2	0·5	5·0
Bed I regenerated by alkali ... Bed II regenerated by alum ...	4·8	4·7	0·8

SUMMARY.

A system of ion-exchange resins comprising of a locally prepared cation-exchanger ('Avaram' resin) and a foreign anion-exchanger (Amberlite IR-4) has been shown to be effective in removing fluorine from waters containing up to 5 parts per million.

The efficiency of fluorine removal by Amberlite IR-4 is influenced by the efficiency with which the primary bed of the cation-exchanger works and also by the total salt content of the raw water.

Alum-treated cation-exchange resin from 'Avaram' bark can be used as an effective material for removing fluorides from water. The use of this material possesses several advantages over the ion-exchange systems in that (*i*) only one bed is used, (*ii*) we dispense with the anion-exchange resin which is difficult to obtain, and (*iii*) we use a familiar chemical as alum for regeneration instead of acid and alkali.

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