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THE DEVELOPMENT AND USE OF THE BONE FILTER FOR REMOVING FLUORINE FROM DRINKING WATER

By
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TABLE OF CONTENTS

ILLUSTRATIONS

THE DEVELOPMENT AND USE OF THE BONE FILTER FOR REMOVING FLUORINE* FROM DRINKING WATER

By
H. V. Smith and W. B. Davey

INTRODUCTION

Since the discovery in 1931 (35) that the presence of fluorine in drinking water is the cause of mottled enamel in human teeth the problem has been one of the major projects of the Department. The plan of research was divided into definite phases—namely, (1) a study and selection of reliable methods for determining fluorine (30) in small amounts, (2) a survey of the waters of the state, and (3) methods of removing fluorine from drinking water.

An extensive survey of the municipal water supplies of this state (31) and an examination of the teeth of the children who had used these waters from birth showed that high concentrations of fluorine produced severe cases of mottled enamel, and lower concentrations, more moderate types of this tooth defect. Very mild cases of mottled enamel were associated with the continuous use of water whose fluorine content was as little as 0.9 p.p.m. (32). Mottled enamel has not been found on the teeth of children who have used water containing 0.8 p.p.m. or less.

In the Salt River Valley (34) extensive investigations were conducted on the fluorine content of ground waters. It was found that fluorine in toxic concentrations very often occurred in water from the shallow wells, while water from the deep wells in the same vicinity was relatively free from fluorine. This suggests the possibility of securing good water by deepening the wells. In other localities there seemed to be no correlation between the depth of wells and their fluorine content.

The areas in the state which are particularly affected lie chiefly along the San Pedro and Gila rivers, in part of the Salt River Valley, and in the Sulphur Spring Valley. Waters containing toxic amounts of fluorine occur in other parts of the state, but they do not assume the importance of those already mentioned. Waters in this state have been found to range in fluorine content from 0.0 to 30.0 p.p.m.

Investigations of fluorine removal methods were delayed somewhat by the insistent local demands for a survey of the waters in the state (27, 28, 29, 30). These surveys in some instances pointed out the possibility of changing to a near-by safe supply. However, in many cases it was impossible to find water containing less than 0.9 p.p.m. of fluorine within a radius of over 10 miles.

*The term "fluorine" is used here to mean fluorides, fluosilicates, or any compound of fluorine found in water.

Hence the necessity of developing an effective and cheap method of treating the water in the home, in schools, and in municipal plants was apparent. Since 1931 there have been several attempts to remove fluorine from water by chemical treatment.

Most proposals have proved ineffective or impractical. Boruff (5) in 1934 used several compounds of aluminum such as aluminum sulphate, sodium aluminate, zeolite, activated alumina, and bauxite in his efforts to free water from toxic amounts of fluorine. The most effective compound was found to be aluminum sulphate. In spite of such precautions as exact *p*H control the necessity of which was pointed out by Kempf, Greenwood, and Nelson (15), the method has proved too erratic and unreliable in behavior, too costly, and therefore impractical.

In the same year McKee and Johnson (19) (patent number 2,072,376) suggested the use of activated carbon. This substance is also costly and is only effective in fluorine removal when the *p*H is 3.0 or below. For this reason activated carbon has never been seriously considered as a practical means of fluorine removal.

Fink and Lindsay (10) in 1937 used activated alumina (Churchill patent number 2,059,553) in the laboratory and reported effective fluorine removal from water. Swope and Hess (36) also reported satisfactory results from the use of this material ("Defluorite"), but its use in tests with several Arizona waters in the field were highly unsatisfactory.

In 1937 Scott *et al.* (25) reported a lowering of the fluorine concentration of waters after they had been softened by the lime-soda process. It was found that this treatment was more effective if the magnesium content of the water was high originally, or if magnesium salts were added to the water before softening. However, the addition of lime to the water in sufficient quantities to be effective in fluorine removal raised the *p*H of the water to 10.5. Thus the caustic alkalinity of about 30 p.p.m. must be destroyed by carbonation. Again the method is not effective if the fluorine content is higher than 3.3 p.p.m. For these reasons the usefulness of the method is limited.

Work in the laboratory at the University of Arizona has centered around the use of bone or other forms of carbonate apatite in fluorine removal as first suggested by W. T. McGeorge of this station.

Chemical analyses as well as X-ray diffraction examinations indicate that bone is a carbonate apatite with the probable formula of $3Ca_3(PO_4)_2 \cdot CaCO_3$ or $3Ca_3(PO_4)_2 \cdot CaCO_3 \cdot H_2O$ (3, 4, 6, 7, 13, 14, 16, 17, 22, 23). Since Gassmann (12) has pointed out that carbonate apatite has the power of anion exchange, it is logical to believe that fluorine might in some measure replace the carbonate radical in the carbonate-apatite, the hydroxyl radical in hydroxy-apatite, and chloride in chlorapatite with the formation of fluorapatite, the completeness of replacement probably depending on the time of contact and the fineness of subdivision of the adsorbing material. It has been shown by Murray and Renard (20) and Carnot (6) that animal bones contain fluorine and that the amount

varies with the intake of fluorine and that fossil bones or bones which have been in contact with a water containing fluorine have a particularly high fluorine content. Hendricks *et al.* (14) state that "upon fossilization, the carbonate group and the water molecule of carbonate apatite are replaced by fluorine." With these assumptions in mind and with the knowledge that treated bone would remove fluorine from water, a study was begun of the details of the reaction, the preparation, and the effectiveness of bone in removing fluorine from water.

Preliminary work in this laboratory in 1933 showed that bone could actually remove fluorine from water, although without special treatment it was not as highly effective as desired. Since that time methods of treatment of bone to increase its efficiency in defluorinating drinking water have been constantly investigated. In 1937 a brief report of the outcome of these investigations appeared in *Water Works Engineering* (33). Since that time further refinements of the method for treatment of bone and development of it for use in a practical bone filter for fluorine removal have been made. It is the purpose of this paper to discuss the research which led to the development of this filter.

During the course of this work reports from other laboratories of the effectiveness of similar compounds have appeared. Adler, Klein, and Lindsay (1) have prepared a synthetic phosphate compound of a composition similar to bone which is effective in fluorine removal.

MacIntire and Hammond (18) suggest precipitating calcium phosphate from phosphoric acid and lime in a fluorine-containing water as a means of removing the fluorine. Several trials in this laboratory however have shown the method to be ineffectual. Clark and Mann (8) have reported successful fluorine removal by the use of bone ash.

EXPERIMENTAL

At the present time there are several satisfactory analytical methods used for determining fluorine.

This was not true in 1931 when the first fluorine determinations were made at this station (35). At that time a modification of the volatilization method of Reynolds, Ross, and Jacobs was used. This method was tedious and not well adapted to the analysis of water. In this present work two methods of analysis were chosen. The Sanchis method was used wherever possible because of its simplicity, but whenever interfering ions were found which would vitiate the results, the more complicated Willard and Winter (37) method of analysis was used. In order to determine under what conditions the Sanchis method could safely be used, a study was made of the effect upon the method of various ions commonly found in water. This study was confined to the effect of phosphates, sulphates, chlorides, calcium, and bicarbonates.

Standard fluorine solutions were prepared and equilibrated with solutions of the above ions of different concentrations.

Samples were then removed and the fluoride content determined by the Sanchis method. A comparison of the results thus obtained was then made with the values found for those solutions containing only fluorine.

TABLE 1.—EFFECT OF THE PHOSPHATE ION ON THE SANCHIS METHOD.

Initial fluorine* (p.p.m.)	Phosphate* added (p.p.m.)	Final fluorine (p.p.m.)
0.0	0.0	0.0
0.0	2.0	0.0
0.0	5.0	0.0
0.0	10.0	0.0
0.0	15.0	0.0
0.0	20.0	0.0
0.0	25.0	0.0
0.5	0.0	0.5
0.5	2.0	0.5
0.5	5.0	0.5
0.5	10.0	0.5
0.5	15.0	0.4
0.5	20.0	0.2
0.5	25.0	0.1
1.0	0.0	1.0
1.0	2.0	1.0
1.0	5.0	0.9
1.0	10.0	0.9
1.0	15.0	0.8
1.0	20.0	0.3
1.0	25.0	0.2
1.5	0.0	1.5
1.5	2.0	1.5
1.5	5.0	1.4
1.5	10.0	1.4
1.5	15.0	1.35
1.5	20.0	0.95
1.5	25.0	0.8
2.0	0.0	2.0
2.0	2.0	2.0
2.0	5.0	1.9
2.0	10.0	1.85
2.0	15.0	1.6
2.0	20.0	1.2
2.0	25.0	1.1

*PO_4 added as $Na_3(PO_4)_2$; F added as NaF.

The effect of the phosphate ion is shown in Table 1. It will be noted that as the phosphate concentration increases, the results obtained show an apparent decrease; and the effect of the phosphate ion is more pronounced when the fluorine concentration is greatest. For example, when the initial fluorine content was 0.5 p.p.m., the addition of 25 p.p.m. of phosphate showed only 0.4

p.p.m. of fluorine; but when the initial fluorine concentration was 2.0 p.p.m., the addition of 25 p.p.m. of phosphate decreased the apparent fluorine content to 1.1 p.p.m. However when the concentration of the phosphate ion is under 10.0 p.p.m. little change in the actual fluorine content is noted. This was chosen as the upper limit of phosphate concentration for use of the Sanchis method. Whenever coagulation of the indicator occurred, the water was analyzed for phosphate by the ammonium molybdate-stannous chloride method. If the phosphate concentration exceeded 10 p.p.m., the sample was reanalyzed for fluorine by the Willard and Winter distillation method. This procedure was found necessary on only a few samples since the maximum solubility of the treated bone with respect to the phosphate ion is in the neighborhood of only 3 p.p.m. However, on certain laboratory and field studies involving the synthetically prepared tricalcium phosphate, Defluorite, it was necessary to use the distillation method since the solubility of this material with respect to the phosphate ion is much greater, often as high as 200 p.p.m.

An investigation of the effect of chloride, sulphate, calcium, and bicarbonate ions on the Sanchis method showed them to be much less of a factor in vitiating the fluorine results than was the phosphate ion. Table 2 shows that calcium, chloride, and bicarbonate ions have practically no effect up to concentrations of 500 p.p.m., but that the sulphate ion gives high fluorine results in concentrations of 500 p.p.m. or over. This is in substantial agreement with the work of both Sanchis (24) and Scott (25).

TABLE 2.—EFFECT OF VARIOUS IONS ON THE DETERMINATION OF FLUORINE* BY THE SANCHIS METHOD.

Ion added	Concentration of ion added (p.p.m. F)	Final concentration of fluorine (p.p.m.)
Sulphate as Na_2SO_4	0	0.5
	100	0.5
	200	0.5
	500	0.7
	1,000	0.8
Chloride as NaCl	0	0.5
	100	0.5
	200	0.5
	500	0.5
Calcium as $CaCl_2$	0	0.50
	25	0.45
	50	0.40
	100	0.50
	200	0.45
Bicarbonate as $NaHCO_3$	0	0.50
	50	0.50
	100	0.45
	200	0.45
	500	0.45

*Initial concentration of fluorine=0.5 p.p.m.; fluorine present as NaF.

PRELIMINARY TREATMENT, ACTIVATION, AND REGENERATION OF BONE

The bone used throughout the studies conducted was ordinary beef bone. In practically every case the bone had been boiled or steamed to remove most of the fat, protein, and other organic materials and had been ground to at least ¼-inch size. In the laboratory the bone was further crushed and boiled with alkali (about 2*N*) to remove more completely the organic material present. This treatment was continued until the bone had lost its flinty characteristics and had become snow white in appearance. The bone was then washed in water, dried, and graded in fineness. The graded fractions were again treated with alkali, washed with water, the excess alkali neutralized with dilute hydrochloric acid (about 0.25*N*), washed again with water, and dried. Bone treated in this manner now shows its maximum capacity for removing fluorine from water.

The initial activation of the bone with alkali and acid suggested the possibility of regeneration of the material after its capacity for removing fluorine from water had been exhausted. Experiments conducted on this spent bone showed that it could be reactivated by treating with sodium hydroxide and hydrochloric acid just as in its initial preparation. The principle of the activation seems to be the same in each case—a preliminary treatment with a base, followed by neutralization with an acid. It has been found that practically any base-acid combination will produce a rejuvenated bone. Experiments conducted with sodium hydroxide followed by a treatment with lactic, tartaric, oxalic, citric, phosphoric, boric, formic, acetic, propionic, carbonic, hydrochloric, sulphuric, and nitric acids all have produced a bone of practically the same fluoride-removing power. Results of this study are shown in Table 3.

If bone from different sources or bone prepared in different ways is to be compared for its fluorine-removing ability, some

TABLE 3.—EFFECT OF REGENERATION OF BONE (40-60 MESH) WITH VARIOUS ACIDS OF POTENCY VALUE (POTENCY VALUES IN P.P.M. FLUORINE).

Acid used*	Time of contact (hours)		
	½	2	24
Lactic	0.40	0.40	0.40
Tartaric	0.45	0.35	0.40
Oxalic	1.10	0.90	1.00
Citric	0.40	0.50	0.45
Phosphoric	0.50	0.45	0.50
Boric	0.60	0.65	0.60
Formic	0.40	0.45	0.40
Acetic	0.40	0.35	0.45
Propionic	0.40	0.40	0.50
Hydrochloric	0.50	0.60	0.50

*0.2*N*.

basis of comparison must be devised. The method of comparison which was developed was called the "standard potency test." This test consists of shaking 2 grams of the material for 1 hour in an end-over-end shaker (15 r.p.m.) with 500 cc. of 3.0 p.p.m. fluorine solution made up in distilled water. The mixture is immediately filtered and the residual fluorine determined in the filtrate, usually by the Sanchis method. By using this purely arbitrary method, a comparison of products may be made in the laboratory. The so-called "potency" value, as defined here refers to the residual fluorine left in the solution after the shaking has taken place.

Referring again to Table 3 it is found that the sodium hydroxide treatment (hot), followed by neutralization with the various

TABLE 4.—EFFECT OF STRENGTH OF ACID ON REGENERATION OF BONE (40-60 MESH).

Acid used	Concentration of acid used (normality)	Time of contact of bone and acid (minutes)	Percentage loss	Residual F potency (p.p.m.)
Acetic.....	0.001	5	3.5	1.1
		10	7	1.0
		30	9	0.9
	0.005	5	7	0.9
		10	10	0.9
		30	11	0.9
	0.01	5	8	0.9
		10	9	0.9
		30	10	0.9
	0.05	5	8	0.9
		10	10	0.9
		30	14	0.9
	0.10	5	10	0.9
		10	13	0.9
		30	14	0.9
	0.20	5	17	0.9
		10	20	0.8
		30	22	0.8
Hydrochloric.....	0.05	5	17	0.9
		10	18	0.9
		30	20	0.9
	0.10	5	15	0.9
		10	18	0.8
		30	21	0.8
	0.20	5	17	0.8
		10	21	0.8
		30	23	0.8

acids mentioned, results in a bone product of practically the same fluoride-removing value or "potency" value in each case. However, regeneration by this method was accomplished with a fairly high percentage loss of bone. This dissolution loss led to a study of the minimum concentrations of alkali and acid necessary for reactivation as well as the conditions best suited to a rejuvenation of the bone in an effort to reduce these losses.

A series of experiments was first set up to study the minimum concentration of acid that could be used. A quantity of bone was boiled for several hours with 0.5*N* sodium hydroxide solution, washed and dried. Samples of this material were treated with acetic acid ranging in concentration from 0.001*N* to 0.2*N* and with hydrochloric acid ranging from 0.05 to 0.2*N*. The time of contact of acid and bone was varied, and the percentage loss noted in each case. Results of this study are shown in Table 4. The results show that the strength of acid used is not important as long as sufficient acid is present to neutralize the excess alkali used in the preliminary treatment. The potency values obtained with the more dilute concentrations are practically the same as with the higher concentrations. Any excess acid seems to react with the carbonate of the bone thereby creating a greater percentage loss on regeneration. The time of contact of the bone and the acid, also, does not appear to be of importance as long as sufficient time is allowed for neutralization to occur. A 5- to 10-minute treat-

TABLE 5.—EFFECT OF VARYING ALKALI CONCENTRATION ON THE REGENERATION OF BONE (40-60 MESH) BY BOILING WITH SODIUM HYDROXIDE.

Strength of NaOH used (normality)	Time of treatment (minutes)	Percentage loss from NaOH	Total percentage loss alkali and acid*	Residual F potency (p.p.m.)
0.01	5	3.6	14.0	2.7
	15	6.4	10.8	2.5
	30	4.0	11.2	2.0
	60	7.0	11.6	2.2
0.05	5	3.6	9.2	2.0
	15	2.4	15.6	2.0
	30	2.8	14.0	1.7
	60	5.2	18.8	1.7
0.10	5	5.6	12.8	1.6
	15	7.0	12.5	1.7
	30	8.0	14.0	1.6
	60	10.0	15.6	1.5
0.20	5	7.2	12.8	1.4
	15	7.6	13.2	1.3
	30	8.0	11.2	1.4
	60	10.4	18.8	1.3

*Neutralization of the excess base was made by treatment with 0.10*N* acetic acid for 10 minutes.

ment with acid has been found to produce a reactivated bone and at the same time reduce the loss due to dissolution.

The second step in this study was the determination of the strength of alkali necessary for rejuvenation of the bone. It has been found that the sodium hydroxide treatment is the most important step in the reactivation process. A series of experiments was set up using bone which had lost its capacity for removing fluorine. Samples of this material were treated with various concentrations of alkali for different periods of time. The experiment was conducted by boiling the bone with the alkali in one case and by treatment in the cold in the second case. The percentage loss on alkali treatment, the total percentage loss on alkali and acid treatment, and the potency value of each product was also determined. Neutralization of the excess alkali was accomplished in each case by treatment with 0.1*N* acetic acid for 10 minutes. The results of the experiment are shown in Tables 5 and 6.

TABLE 6.—EFFECT OF VARYING ALKALI CONCENTRATION ON THE REGENERATION OF BONE (40-60 MESH) IN THE COLD WITH SODIUM HYDROXIDE.

Strength of NaOH used (normality)	Time of treatment (minutes)	Percentage loss from NaOH	Total percentage loss alkali and acid*	Residual F potency (p.p.m.)
0.01	5	0.0	8.0	2.8
	15	1.2	7.6	2.5
	30	2.3	9.2	2.5
	60	6.0	11.6	2.4
0.05	5	1.2	10.8	2.0
	15	2.0	10.4	1.9
	30	4.8	14.4	1.8
	60	3.2	14.0	1.8
0.10	5	0.4	6.2	2.4
	15	3.2	13.2	2.5
	30	8.0	14.4	2.0
	60	4.8	14.0	1.6
0.20	5	2.8	7.6	1.8
	15	6.4	11.2	2.0
	30	6.0	13.2	2.0
	60	6.8	12.9	1.5
0.01	960	1.0	4.6	2.2
0.05	960	2.0	7.2	1.6
0.10	960	2.4	10.0	1.3
0.20	960	2.8	12.0	0.9

*Neutralization of the excess base was made by treatment with 0.10*N* acetic acid for 10 minutes.

It appears that reactivation with the sodium hydroxide in the cold results in a product equally as good as that obtained by boiling with the alkali, and, in addition, the solubility loss is less. In marked contrast with the acid treatment, however, it was found that the strength of base used and the time of contact necessary was much greater. But, since the solubility loss in the cold with the alkali is much less than that obtained with the acid, a 24-hour treatment with a stronger base is not out of the question. The added fluoride-removing power of bone treated for longer periods of time with greater strengths of base more than compensates for the solubility losses which may occur. The total percentage loss for reactivation in the cold with 0.2*N* NaOH and 0.1*N* acetic acid has been found to be from 10 to 12 per cent. This loss by dissolution may be somewhat decreased, however, by using carbon dioxide gas for the purpose of neutralization. Experiments conducted using this method have shown that the average loss may be decreased to 1 or 2 per cent.

Results showing the neutralization of the sodium hydroxide-treated bone by bubbling carbon dioxide gas through a suspension of the material are shown in Table 7, together with the potency value obtained and the percentage loss on reactivation. Since the product obtained under this treatment is as effective in removing fluorine as that obtained by using stronger acids and the percentage loss is markedly decreased, this procedure may be recommended for reactivation purposes.

TABLE 7.—EFFECT OF CARBON-DIOXIDE GAS ON REGENERATION OF BONE (40-60 MESH).

Treatment	Total percentage loss	Residual F (p.p.m.)
Boiled with NaOH; washed with water; carbon dioxide passed for 15 minutes.....	4.9	0.9
Treated with NaOH in cold for 20 hours; washed with water; carbon dioxide passed for 15 minutes.....	1.8	1.0

CALCINATION STUDIES

It is recognized that the removal of fluorine by bone is a surface reaction and that if the surface is increased, the effectiveness of the bone in removing fluorine from water is likewise increased. A greater surface area may be obtained by grinding the material, but this procedure has a serious limitation—namely, the flow of water through the finely ground bone is decreased so much that the use of this material becomes impractical in most types of filters except perhaps certain pressure filters. Another procedure commonly used for increasing surface area without decreasing the state of subdivision of the bone is the process known as calcination. This merely involves the heating of the bone at a high temperature for a short period of time. Calcination removes the

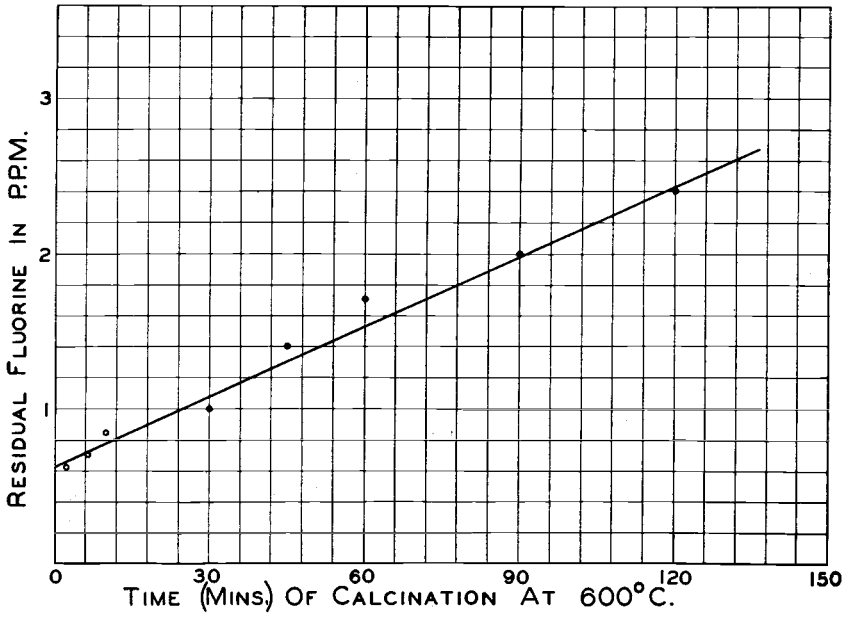

Figure 1.—Effect of calcination on the fluoride-removing power of bone.

volatile material in the pores of the bone and causes a certain amount of decrepitation which has the effect of increasing the surface area of contact.

A number of samples of alkali-acid activated bone (20-40 mesh) were heated in silica crucibles at different temperatures, and standard potency tests made on the products. The results are shown in Figure 1. An examination of the data shows that calcination of bone for short periods of time effects little change in the fluoride-removing power but that on prolonged heating, especially at higher temperatures, a marked decrease in the potency of the bone is obtained. It was thought that perhaps a more uniform heating together with the constant supply of moisture would be desirable, and a better product would be obtained. For this purpose a small rotary kiln was constructed. This apparatus was so designed that it would fit into an electric muffle and could be rotated constantly throughout the heating process. Steam was supplied continuously to the system through a hole in the muffle door. The kiln was placed in the furnace, brought to the desired temperature, and the bone then added and heated with constant rotation for the predetermined period of time. Standard potency tests conducted on the material prepared in this manner were disappointing (Table 8). The bone products did not show as great a fluoride-removing power as bone treated in the dry state, and, hence, this steam process was abandoned as an unnecessary step in the preparation of the bone.

TABLE 8.—EFFECT OF CALCINATION ON THE FLUORIDE-REMOVING POWER OF BONE.

Treatment	Temperature of calcination (°C.)	Time of heating (minutes)	Residual F potency (p.p.m.)
Original bone	.....	.....	0.60
Calcination in air	200	2½	0.85
		5	0.75
		10	0.70
		30	0.65
		45	0.65
		60	0.65
		120	0.60
	400	2½	0.60
		5	0.60
		10	0.60
		30	0.70
		45	0.70
		60	0.70
		120	1.10
	600	2½	0.62
		5	0.70
		10	0.85
		30	1.00
		45	1.40
		60	1.70
		90	2.00
Calcination with steam	350	10	1.40
	400	10	1.50
	600	2	1.20
		5	1.25
		10	1.35
		15	1.60

TABLE 9.—EFFECT OF ACID TREATMENT ON CALCINED BONE (40-60 MESH).

Calcination treatment	Acid treatment	Residual F p.p.m.
10 min. at 200° C.	20 hours with 0.2*N* HCL	0.50
2 hours at 200° C.	20 hours with 0.2*N* HCL	0.70
10 min. at 400° C.	20 hours with 0.2*N* HCL	0.40
2 hours at 400° C.	20 hours with 0.2*N* HCL	0.60
10 min. at 600° C.	20 hours with 0.2*N* HCL	0.40
2 hours at 600° C.	20 hours with 0.2*N* HCL	0.70
Unheated bone	20 hours with 0.2*N* HCL	0.60

It was thought that possibly during the heating process the bone was converted to the oxy- or hydroxy-apatite and that, therefore, a treatment with hydrochloric acid was necessary to render the bone potent again. Consequently, several representative portions of the calcined bone were treated with dilute hydrochloric acid, and standard potency tests were made on the products obtained. Results of the treatment are shown in Table 9.

The acid after-treatment produces a slightly more potent bone when applied to bone heated for 10 minutes; calcination for 2 hours followed by the acid after-treatment produced a less effective product. Over the range of temperatures studied it is to be noted that the best calcined products are those that have been heated at the higher temperatures for short periods of time.

Further study has shown that short-time treatments with acid are as effective as the 20-hour treatment used in the first study (Table 13). Results of these "flash" acid treatments are shown in Table 10. Calcination of bone for 10 minutes at 400 to 600 degrees C. followed by a 5 to 15 minute acid treatment has been found to yield a good bone product for the fluoride removal process.

TABLE 10.—EFFECT OF SHORT-TIME ACID TREATMENTS ON THE FLUORIDE-REMOVING POWER OF CALCINED BONE (40-60 MESH).

Time of calcination at 600° C. (minutes)	Acid treatment (minutes)	Residual F potency (p.p.m.)
	0.1*N* HCl	
10	5	0.50
	15	0.60
	30	0.60
	60	0.50
	180	0.65
	0.2*N* HCl	
10	5	0.60
	15	0.75
	30	0.80
	60	0.80
	180	0.75

It was found by Reynolds, Jacob, Rader, and Marshall (21) that in the presence of sufficient silica and water vapor, heating phosphate rock for 30 to 60 minutes at 1,400 degrees C. results in the volatilization of 95 to 100 per cent of the fluorine and conversion of 85 to 95 per cent of the phosphorus into the citrate soluble condition. Since nearly all of the fluorine is driven off in the process, it was thought that perhaps the rock would function in removing fluorine from water. Potency tests conducted on the defluorinated rock phosphate furnished by Jacob were disappointing (Table 11). Treatment of this material with alkali and acid as used on the activation of bone also gave unsatisfactory results.

TABLE 11.—EFFICIENCY OF DEFLUORINATED ROCK PHOSPHATE (20-40 MESH) IN REMOVING FLUORINE FROM WATER.

Weight of rock (grams)	Mesh	Initial F (p.p.m.)	Residual F (p.p.m.)
2	20-40	3.0	2.3
10	20-40	3.0	2.2

The greater fluoride-removing power which calcination gives the bone would hardly warrant the cost of this additional step, however, if this procedure had not been found necessary for the preparation of a suitable material for use in a filter. There are two reasons why this process has been found necessary: (1) it makes bone more easily wettable, and (2) it prevents microbial growth in the filter.

It was noted that on certain occasions the bone activated by the usual alkali-acid treatment refused to measure up to expectations in regard to the fluoride-removing power. This decrease in potency was found to be caused by the nonwetting of the bone. Often the prepared material would float on the top of the water. In other instances the bone would seemingly be wetted, but on closer observation it was noticed that each bone particle was enclosed in a tiny air bubble. Obviously under these conditions the effectiveness of the bone was reduced. The reason for this nonwettability of the bone may probably be explained on the basis of the presence of an oil film around the bone particles. It is most likely that these bone products which refuse to wet have a film, perhaps only monomolecular, of oil surrounding each particle and, hence, the reason for the nonwetting. The calcination process evidently destroys this film, since all products prepared in this manner have wetted easily and quickly.

STUDIES ON THE PUTREFACTION OF BONE

The second reason for the necessity of calcination, that of preventing microbial growth to develop in the bone, is more important and would alone more than make up for the added cost of this procedure. A number of laboratory and field studies have shown that uncalcined bone has a tendency to putrefy and thus to impart a disagreeable odor and taste to the water. This effect generally appears after the filter has been used for some time and is then allowed to remain inactive for several days. Also moist samples of bone left undisturbed in the laboratory have produced evidences of putrefaction.

A few attempts made to isolate the responsible organism or organisms proved unsuccessful. The organisms, however, have been shown to be anaerobic or semianaerobic, since the putrefaction develops only in bone covered with water or in the lower portion of a moist column of bone. The microorganisms and malodor which they develop may be quickly destroyed by ex-

posure to light and air and allowing the bone to dry. Preliminary results indicate that some type of mold is responsible, since only those organisms which grew on mold media produced a similar growth when inoculated into bone. Various types of culture media were prepared and inoculated with a suspension of the infected bone and with the infected bone itself. The typical organisms which developed were reinoculated into Noguchi tubes filled with moist, sterile bone. The Noguchi tube is a long, narrow test tube specially designed such that when filled with moist bone, anaerobic conditions develop in the lower portions, and aerobic conditions towards the top of the tube. The lower portions of the bone in the Noguchi tubes, when inoculated by means of a long needle with the material immediately surrounding the bone on the mold media, produced evidences of similar growth as was noted in the field units and in the laboratory. Putrefaction of sterile bone also could be brought about by covering the bone with water and inoculating with the infected material. Sterilization of the bone with a number of common sterilizing agents such as hydrogen peroxide, chlorox, and hypochlorite were tried, and, although these agents would quickly clear up the condition on the first application, putrefaction would again develop after use of the bone. However, calcined bone has never shown any tendency to putrefy. Inoculations which have quickly produced putrefaction in the case of uncalcined bone have never caused any growth of microorganisms to develop on calcined bone. The results of a few of such inoculations are shown in Table 12.

TABLE 12.—EFFECT OF INOCULATIONS OF CALCINED AND UNCALCINED BONE.

Source of bone	Treatment	Time of inoculation	Time of putrefaction
Eagle Milling Co., Tucson, Arizona	Alkali-acid-calcined	2/ 1/39	No growth at 5/ 7/39
Eagle Milling Co., Tucson, Arizona	Alkali-acid-calcined	2/ 1/39	No growth at 5/ 7/39
Eagle Milling Co., Tucson, Arizona	Alkali-acid-no calcination	2/15/39	2/18/39

Extensive field tests have been carried on with calcined material and, as yet, not one case of putrefaction has occurred.

Why calcination prevents the growth of microorganisms on the bone may in all probability be explained on the basis of the change which the organic matter content undergoes at these temperatures. The organic matter at these high temperatures is probably changed by pyrolysis, dehydration, and oxidation to a form which will not support the growth of microorganisms.

In addition to rendering the bone wettable and nonputrefactive, there are several added advantages of calcination: (1) the bone is made harder and less subject to losses by attrition and dissolution; (2) the surface area is increased, thus increasing the capacity

of removal; and (3) more fluorine is removed from the bone (see Chemical Analysis) which also increases its fluoride-removing power.

CHEMICAL ANALYSIS OF BONE

It is a well-known fact that the CaO-P_2O_5 ratio in bone is greater than that required for tricalcium phosphate (2, 11, 12, 17, 22). There has long been a controversy as to the chemical composition of bone. Klement and Tromel (16) give the formula of bone as $3Ca_3(PO_4)_2 \cdot Ca(OH)_2 + CaCO_3$. Gassmann (12) gives evidence that the structural part of bone is as Werner suggested—$3Ca_3(PO_4)_2 \cdot CaCO_3$. Bassett (3) believed that the formula was probably $Ca_{10}(OH)_2(PO_4)_6$, with amorphous or crystalline $CaCO_3$. The X-ray observations of DeJong and others (9, 23) showed that the principal constituent of bone was an apatitelike substance. Hendricks, Hill, Jacob, and Jefferson (14), as a result of microscopical and X-ray diffraction examinations, report that bone is probably essentially a carbonate apatite and that for structural reasons it is probably $Ca_{10}CO_3(PO_4)_6 \cdot H_2O$. Several representative samples of bone were analyzed not for the purpose of determining a formula but to obtain an idea of the true bone content of the product. It was found that the values obtained for the percentage of CaO and P_2O_5 were lower in every case than the calculated theoretical percentages, assuming the formula to be that of carbonate-apatite or the hydrated carbonate-apatite as suggested by Hendricks. This may probably be explained by assuming that the threatment given the bone in the course of its preparation is not rigorous enough to remove all impurities present; a small amount of organic matter and possibly some other materials are present. The alkali-acid calcination treatment removes practically all impurities, at least to such an extent as to render the product safe for use in a bone filter. The results of the analysis for calcium, phosphorus, and fluorine are shown in Table 13, together with theoretical values calculated for several suggested formulas for bone and for fluorapatite.

TABLE 13.—CHEMICAL ANALYSIS OF BONE (DRY BASIS).

Type of bone and treatment received	CaO (%)	P_2O_5 (%)	Ratio $CaO:P_2O_5$	F (%)
Raw chipped bone untreated	24.30	31.09	0.782	0.313
Chipped bone (alkali-acid)	42.84	40.28	1.063	0.228
Chipped bone (alkali-acid-F saturated)	41.58	36.44	1.144	1.912
Chipped bone (alkali-acid-calcined-acid treated)	41.72	37.09	1.124	0.174
Theoretical—$Ca_{10}(CO_3)(PO_4)_6$	54.33	41.27	1.316	.....
Theoretical—$Ca_{10}(CO_3)(PO_4)_6 \cdot H_2O$	53.39	40.56	1.313	.....
Theoretical—$Ca_{10}F_2(PO_4)_6$	54.56	42.06	1.297	3.76

The ratio of CaO to P_2O_5 should be the same approximately as that calculated from the theoretical percentage regardless of im-

purities present, unless such impurities present in the bone are in the form of some other calcium and phosphorus compound. However, results show that the CaO-P_2O_5 ratio is lower in each case, indicating that more calcium is being dissolved during the activation and preparation of the bone.

A number of bone samples from different sources as well as several rock phosphates were analyzed for fluorine in order to determine the average fluorine content of these materials both in the natural state and in the treated form. It will be noted that the alkali-acid treatment results in a decrease of the fluoride content and that calcination results in a still further decrease. The rock phosphate samples show a high content approaching the theoretical of fluorapatite. Also while saturation with fluorine under the conditions of the experiment (equilibrating with a high NaF concentration for several days) did not reach the value calculated from fluorapatite, the fluoride content was substantially higher than that of the treated bone. Results of the analysis are shown in Table 14. It will be noted that the fluoride content of bone after use in a filter has increased somewhat.

TABLE 14.—FLUORINE CONTENT OF BONE AND ROCK PHOSPHATE (DRY BASIS).

Material and treatment	F (%)
Florida rock phosphate (raw)	3.385
Florida rock phosphate (calcined)	3.770
Florida rock phosphate (raw-alkali-acid treated)	3.360
Florida rock phosphate (calcined-alkali-acid)	3.695
Steamed bone meal poultry feed (untreated)	2.363
Apatite	0.075
Calcined bone (F saturated)	0.623
Calcined bone (calcined moist-acid treated)	0.205
Calcined bone (calcined moist-F saturated)	0.720
Calcined bone (after use in filter-capacity lost)	0.396

A number of different bone samples were analyzed for their protein content (nitrogen $\times$ 6.25) in order to determine in some measure the purity of the bone and its susceptibility to putrefaction, it being assumed that the protein content would parallel the rate and degree of putrefaction. It was found that the alkali-acid treatment substantially reduced the organic matter content. However, calcination reduced the protein content only a slight additional amount. As stated before, the small amount of organic matter left in the bone is probably changed in form or the quantity becomes negligible, and, hence, no putrefaction occurs. Results of the analysis are shown in Table 15.

TABLE 15.—PROTEIN CONTENT OF BONE (AIR-DRY BASIS).

Material	Source	Treatment	Protein N × 6.25 (%)
Steamed bone meal	Consolidated Chemical Industries, San Francisco, Cal.	Alkali-acid	0.42
Chipped bone	Swift and Co., Ft. Worth, Texas	Alkali-acid	0.66
Raw bone	Swift & Co., St. Paul, Minn.	Alkali-acid	0.91
Calcined bone	Eagle Milling Co., Tucson, Arizona	Alkali-acid-calcined-acid	0.47
Digesta bone	Glendale, Arizona	Alkali-acid	0.41
Steamed bone meal	Eagle Milling Co., Tucson, Arizona	Alkali-acid	0.56
Steamed bone A	Glendale, Arizona	Alkali-acid	0.84
Steamed bone B	Glendale, Arizona	Alkali-acid	0.81

EFFECT OF MESH ON FLUORINE REMOVAL AND FLOW RATES

The effect of fineness of subdivision of the bone with respect to the amount of fluorine removed was investigated and, as expected, was found to play an important role. A quantity of bone was prepared by the alkali-acid method and segregated into various meshes. Two-gram portions of the different sizes were shaken with 500 cc. of a 5 p.p.m. fluorine solution for 1 hour in an end-over-end shaker (fifteen revolutions per minute). The mixtures were immediately filtered and the filtrates analyzed for their residual fluoride content by the Sanchis method. Results of the experiment are shown in Table 16.

TABLE 16.—EFFECT OF BONE MESH ON FLUORINE REMOVAL.

Bone mesh	Weight of bone used (grams)	Initial F content (p.p.m.)	Final F content (p.p.m.)
10- 40	2	5.0	1.2
20- 40	2	5.0	0.7
40- 60	2	5.0	0.4
60- 80	2	5.0	0.3
80-100	2	5.0	0.0
less than 100	2	5.0	0.0

The finer fractions of bone effected a much greater removal of fluorine, indicating that the reaction is a surface phenomenon. However, a finer mesh than 40-60 is considered impractical for use in the bone filter, since the rate of flow becomes too slow. Also loss on regeneration of the bone becomes higher with decrease in the size of particles. A finer mesh than 40-60 may possibly be used in the pressure type of filter. Or a combination of meshes such as 40-80 may be used in the gravity type filter without hindering the penetration of water too much.

In connection with mesh studies the flow rates have been also investigated, the problem being approached from two directions: (1) flow rate as a function of mesh and (2) flow rate as a function of depth of column of bone and the ability to remove fluorine from water.

The first experiments conducted involved the measurement of the rate of flow of water through a 12-inch depth of bone of various screen sizes, the head of water being kept constant at 12 inches in each case. For this study a long, narrow tube 2.25 centimeters in diameter was used. The results are shown in Table 17. As was expected the flow rate decreased markedly with the mesh of bone used.

TABLE 17.—RATE OF FLOW OF WATER THROUGH BONE.

Bone mesh	Flow rate (gal./hr./sq. ft./12 in. column)
10-20	4,190
20-40	712
40-60	427

In the second study conducted on this problem the rate of flow and the fluorine-absorbing power of bone were investigated as a function of the depth of column. Three glass tubes of varying diameters were chosen for the work, the first having a diameter of 0.55 inch, the second 0.86 inch, and the third 1.33 inches. In the first experiment the same amount of bone (20 grams) was placed in each tube, and a solution containing 10 p.p.m. of fluorine was passed through as rapidly as possible by gravity flow, a constant head of water of about 12 inches being maintained in each case. The rate of flow together with the amount of water treated was determined. This latter was determined by sampling the water passed through after every 500 cc., and the residual fluorine content found by using the Sanchis method. Water was passed until the "toxic" limit of 0.9 p.p.m. of fluorine was reached.

The results of the experiment are shown in Table 18. As was expected, the tube of smallest diameter and greatest length of column had the slowest flow rate and, therefore, removed more fluorine from the water. The rate of flow through the large tube was so fast that only a very little fluorine was removed from the solution. The second experiment consisted of filling all three tubes to the same height with bone (9 inches) and noting the amount of water treated and the rate of flow in each case. Results of this study are also shown in Table 18. It will be noted that when the height of bone is the same in all three tubes, the total volume of water treated is not a function of the rate of flow, as in the case of Table 21, but of the total weight of bone present. Also it is of interest to note that the amount of fluorine removed in each case is practically the same when calculated in terms of removal per cubic foot of bone.

TABLE 18.—EFFECT OF FLOW RATE ON FLUORINE REMOVAL (40-60 MESH BONE).

Conditions varied	Diameter of tube (inches)	Height of column (inches)	Weight of bone (grams)	Flow rate (gal./sq. ft./hr.)	Total volume of 10 p.p.m. F water treated (gal./sq. ft.)	Grams F removed per cu. ft. of bone
Height of column and diameter of tube	0.55	6.42	20	320	345.5	55.5
	0.86	2.57	20	300	199.2	50.1
	1.26	1.26	20	703	21.6	8.3
Weight of bone used	0.55	9	30	256	761.8	81.6
	0.86	9	72	248	1,160.1	81.0
	1.33	9	169	219	1,466.1	80.2

EFFECT OF TIME OF CONTACT ON FLUORINE REMOVAL

Since the rate at which any filter removes fluorine from water is of extreme importance, it became necessary to study the effect of time of contact of bone and water in the removal of fluorine. Instantaneous removal, of course, would be ideal, for under this condition the flow of water through the filter bed could be increased to any desired rate. The time of contact, however, was found to play an important part.

Samples of alkali-acid activated bone (20-40 mesh) weighing 2, 3, and 5 grams, respectively, were shaken for 1 hour in an end-over-end shaker with a solution containing 3 p.p.m. of fluorine. The mixtures were immediately filtered and the residual fluoride content determined in each case by the Sanchis method. The amount of phosphate in the filtrate was also determined colorimetrically, using ammonium molybdate and stannous chloride. Experimental results are shown in Figure 2.

It will be noted from the graph (Fig. 2) that a family of curves was obtained much as might have been expected. Complete removal is obtained in each case, although considerable time is required for the 2-gram sample of bone to effect the removal. The toxic concentration of fluorine which will cause mottled enamel has been set at 0.9 p.p.m. fluorine (26). Results show that the bone will reduce the concentration to below this toxic level but that the time of contact is important. This slowness of removal brings to light a fundamental consideration in the use of the bone filter—namely, that the capacity of this material is a function of the time of contact and that the time between regenerations of the bone filter will be increased as the flow rate is decreased. This fact was well brought out in the effect of mesh study (Table 16) where it was found that the longer column of bone removed the greater amount of fluorine.

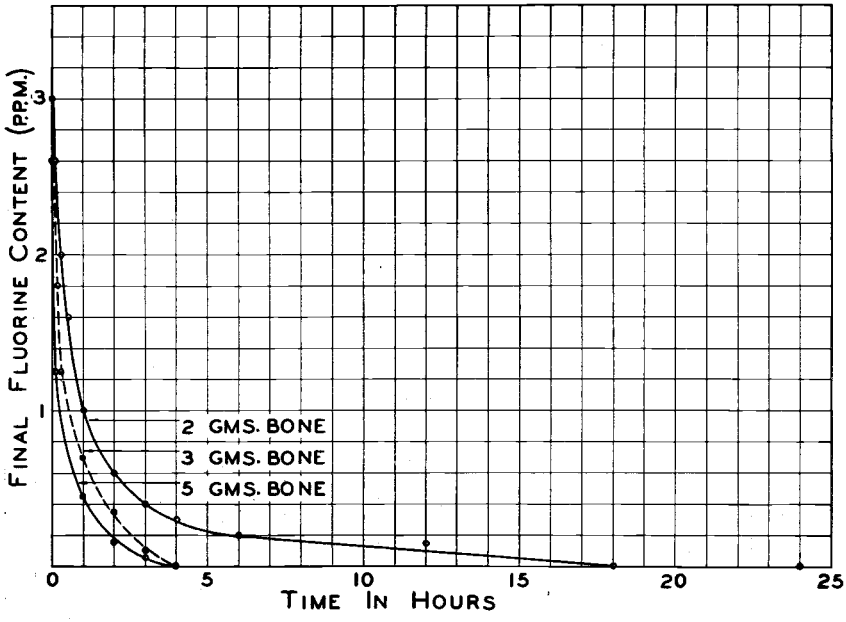

Figure 2.—Effect of time of contact of bone and water in the removal of fluorine.

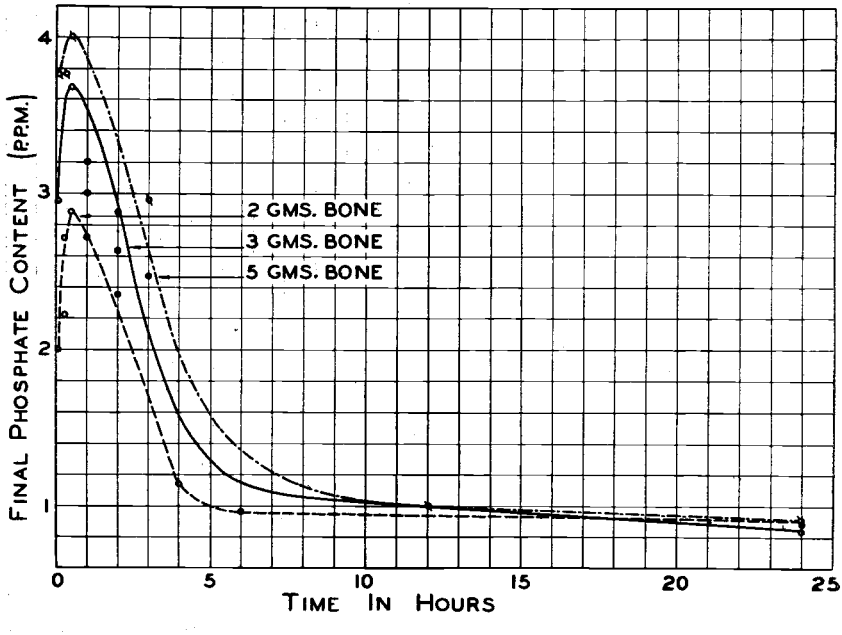

Figure 3—Effect of time of contact on the PO_4 ion dissolved from bone.

In making the above equilibrium studies a number of the samples were analyzed for their phosphate largely as a matter of control, since it has been shown that the presence of more than 5 to 10 p.p.m. of this ion interferes with the accuracy of the Sanchis method. The amount of phosphate dissolved is plotted against the time of shaking (Fig. 3). It will be seen from the graph that there is a rapid initial rise in the phosphate concentration and then a rapid decline, the three weights of bone used giving rise to practically the same final phosphate content. Why more phosphate did not go into solution as the time of contact of the bone and the water increased is difficult to explain. It was thought that perhaps a study of the solubility of the bone with respect to phosphate ion in distilled water and carbon-dioxide-free water might give some clue. Consequently the above experiment was repeated, 3 grams of bone being used.

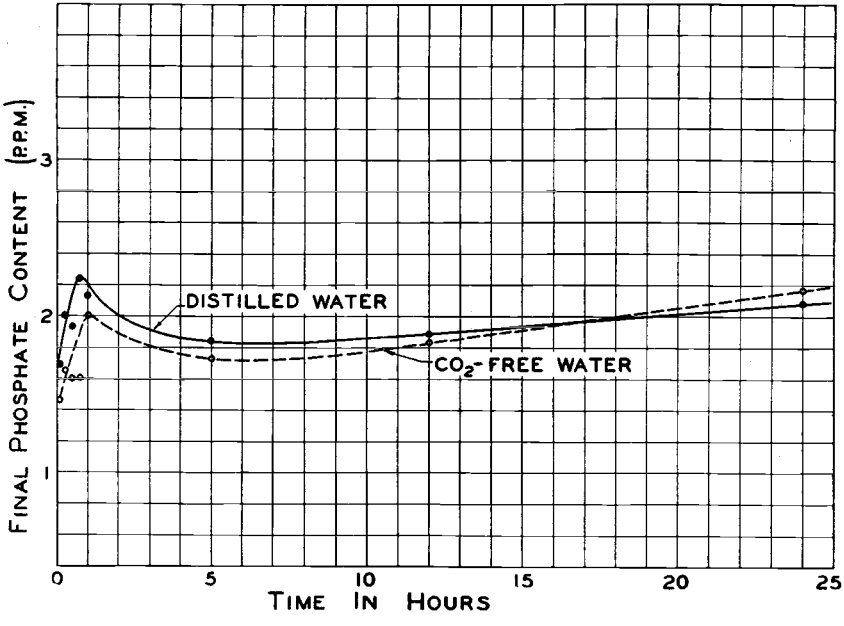

Figure 4.—Effect of time of contact on the PO_4 ion dissolved from bone in distilled water and CO_2-free water.

EFFECT OF *p*H ON FLUORINE REMOVAL

Since in so many of the proposed methods of removing fluorine from water the *p*H played such an important part, it was decided to study this effect in regard to the use of bone. To a series of liter bottles were added 500-cc. portions of a 3 p.p.m. fluorine solution. These solutions were then adjusted to different *p*H values ranging from 3 to 10 by use of the Beckmann *p*H meter and adding dilute hydrochloric acid and sodium hydroxide. The

contents of each bottle were then shaken with 2-gram samples of bone in an end-over-end shaker for 1 hour, the mixtures immediately filtered, and the residual fluorine content of the filtrate determined by the Sanchis method. The final *p*H was also determined. Results are shown in Table 19.

TABLE 19.—EFFECT OF *p*H ON THE REMOVAL OF FLUORINE FROM WATER.

Weight of bone (grams)	Initial *p*H	Final *p*H	Initial F p.p.m.	Residual F p.p.m.
2	3	6.46	3.0	0.65
2	4	6.64	3.0	0.60
2	5	6.93	3.0	0.60
2	6	7.30	3.0	0.60
2	7	7.80	3.0	0.75
2	8	7.95	3.0	0.75
2	9	8.47	3.0	0.90
2	10	10.07	3.0	1.50

It is seen that the *p*H does have an effect on the ability of bone to remove fluorine from water, the amount removed decreasing with increase in *p*H. However, no marked decrease is noted till a *p*H of 9 or higher is reached. Few domestic waters ever attain any such degree of alkalinity, hence the effect is considered unimportant. A rather constant removal is obtained up to a *p*H of about 8, the first change beginning to show around neutrality.

The final *p*H values appear to be significant in that they show that bone has a tendency to bring the reaction mixture to a rather definite value. The average *p*H of bone shaken for 2 hours with a 3 p.p.m. solution is around 7.6. It is noted that there is a tendency for the final *p*H values of Table 19 to approach this value.

The *p*H determinations included in Table 19 (effect of time of contact) are likewise significant. The *p*H values in this case are seen to increase in general with the time of contact. It has been suggested that perhaps this increase may be due to a carbonate ion or a hydroxyl ion which may be replaced somewhat by the fluorine of the water. Assuming that bone is a mixture of carbonate-apatite and hydroxy-apatite, it is not improbable that such a reaction as stated above may be taking place on the surface of the exposed bone.

EFFECT OF TEMPERATURE ON FLUORINE REMOVAL

Since many reactions are known to take place with greater rapidity at higher temperatures, it was decided to investigate the removal of fluorine at different temperatures. For this purpose several quart thermos bottles were used. Standard potency tests with 2-gram portions of bone were conducted in these flasks at different temperatures. Results of the experiment (Table 20) indicate that there was no final temperature effect.

TABLE 20.—EFFECT OF TEMPERATURE ON FLUORINE REMOVAL FROM WATER BY BONE (40-60 MESH).

Temperature* °C	Weight of bone (grams)	Initial F (p.p.m)	Residual F (p.p.m.)
7	2	3.0	0.50
26	2	3.0	0.60
40	2	3.0	0.45
42	2	3.0	0.60
59	2	3.0	0.50
62	2	3.0	0.50
67	2	3.0	0.50
67	2	3.0	0.50
70	2	3.0	0.60

*The temperature variation after shaking was less than 1 degree in each case.

The residual fluorine in each case is practically of the same order of magnitude, the greatest difference being only 0.15 p.p.m. of fluorine. This variation is not considered significant since the accuracy of the Sanchis method is only 0.1 p.p.m. Also the variability of the bone used may account for the difference in some measure.

EFFECT OF SALTS ON FLUORINE REMOVAL

Since it was thought that the mechanism by which bone removes fluorine from water might involve anion exchange, the effect of other salts on the removal was investigated to determine if bone is preferential in its adsorption of fluorine to other anions. The first study on this subject consisted of the addition of various concentrations of chloride and sulphate ions to 500 cc. of a solution containing 3 p.p.m. of fluorine. One- and 2-gram samples of bone were then shaken for 1 hour with this mixture and the residual fluorine content determined in each case by the Sanchis method. Results of the experiment are given in Table 21. Some slight effect is noted in most cases, but if the correction for the sulphate

TABLE 21.—EFFECT OF SULPHATE AND CHLORIDE ON FLUORINE REMOVAL.

Weight of bone (grams)	Initial fluorine (p.p.m.)	Chloride* added (p.p.m.)	Sulphate† added (p.p.m.)	Final fluorine (p.p.m.)
1	3.0	0	0	1.75
1	3.0	500	0	1.80
1	3.0	500	500	2.10
1	3.0	0	500	2.10
2	3.0	0	0	1.10
2	3.0	500	0	1.20
2	3.0	500	500	1.30
2	3.0	0	500	1.60

*Chloride added as NaCl.
†Sulphate added as Na_2SO_4.

ion is applied to the method, the difference observed is only 0.2 to 0.3 p.p.m. The chloride ion appears to have no effect, the greatest variation being only 0.1 p.p.m. which is within the accuracy of the method. The adsorption seems to be preferential, only a slight effect being found with these two salts commonly found in natural waters.

A second study was conducted on this subject using natural waters. Several representative waters of the state of Arizona as well as one water from Illinois were analyzed for their salt content including fluorine. The results of these analyses are given in Table 22.

TABLE 22.—ANALYSIS OF NATURAL WATERS USED IN "SALT EFFECT" STUDY.*

Water	Ca	Mg	CO_3	HCO_3	Cl	SO_4	F
1a. Nine miles west Hayden Junction	22.5	0.0	62.4	578.3	662	520	3.6
2a. Tacna, Ariz.	97.5	127.5	42.0	187.8	681	2,700	3.5
3a. Aledo, Ill.	45.0	18.7	24.0	173.2	214	900	2.5
4a. Agua Caliente hot springs	7.5	11.2	14.4	102.4	273	200	5.0
5a. Mammoth (mine)	22.5	0.0	19.2	153.7	49	40	2.8

*All results are expressed as parts per million. Corrections applied for sulphate ion in each case.

Standard fluorine solutions made up in distilled water were prepared, each solution corresponding in fluoride content to one of the natural waters. To each of the two corresponding water samples (the natural water and the standard) was added an equal amount of bone, the mixtures shaken side by side for 1 hour in an end-over-end shaker, filtered, and the residual fluorine content determined by the Sanchis method. Results of the experiment are given in Table 23.

TABLE 23.—REMOVAL OF FLUORINE FROM NATURAL WATERS AND STANDARD FLUORINE SOLUTIONS OF THE SAME CONCENTRATION.

Water*	Initial F (p.p.m.)	Weight of bone (grams)	Residual F (p.p.m.)
1a	3.6	2	1.30
1b	3.6	2	1.25
2a	3.5	2	1.35
2b	3.5	2	1.25
3a	2.5	2	1.10
3b	2.5	2	0.80
4a	5.0	3	1.50
4b	5.0	3	1.40
5a	2.8	2	1.10
5b	2.8	2	0.80

*a, natural water; b, corresponding standard fluorine solution.

It will be noted that the fluoride-removing power of the bone is slightly decreased in the natural waters, indicating that the adsorption of fluorine by bone is preferential; or, if not preferential, the presence of other ions in the solution has only a slight effect.

EFFECT OF DOUBLE TREATMENT ON FLUORINE REMOVAL

It was suggested that a double treatment of water with smaller portions of bone might prove more effective in fluoride removal than a single treatment with twice as much bone. The double treatment procedure has been found to function well in the extraction of gold by means of activated carbon, and, hence it was tried on fluorine removal by bone. Successive treatments of a standard fluorine solution with two 1-gram samples were compared with results obtained using 2-gram samples. In the case of the double treatment, 500 cc. of a 3 p.p.m. fluorine solution were shaken for 1 hour on an end-over-end shaker with a 1-gram sample of bone, the mixture immediately filtered, and a second 1-gram portion of bone added to the filtrate and shaken again for 1 hour. For purposes of comparison two other 500 cc. volumes of standard fluorine solution were shaken with 2-gram samples of bone for 1 and 2 hours respectively. Residual fluorine in each case was determined by filtering the mixtures and analyzing the filtrate. The results are shown in Table 24.

TABLE 24.—EFFECT OF DOUBLE TREATMENT OF WATER WITH BONE.

Treatment	Initial F (p.p.m.)	Residual F (p.p.m.)
1 gram bone shaken with 500 cc. of solution for 1 hour, filtered, and a second fresh 1-gram portion added and shaken for 1 hour	3.0	0.7
2 grams bone shaken for 1 hour	3.0	0.8
2 grams bone shaken for 2 hours	3.0	0.75

Results indicate that the double treatment is no more effective than the single treatment with twice the quantity of bone being used. It is conceivable, however, that, under conditions where a water is high in fluorine and a considerable demand for water exists, a double pressure-filter-treatment might prove effective in removing greater amounts of the fluorine. For ordinary use the single unit has been found to function satisfactorily.

PHOTOMICROGRAPHS OF BONE

It seemed advisable to gain some knowledge of the structure of bone in connection with the removal of fluorine from water. Consequently, several thin sections of bone were prepared and photographed along with a sample of Defluorite and rock phosphate. The photographs are shown in Plates I to IV, inclusive.

Plate I.—Steamed bone meal, 40-60 mesh, original untreated sample.

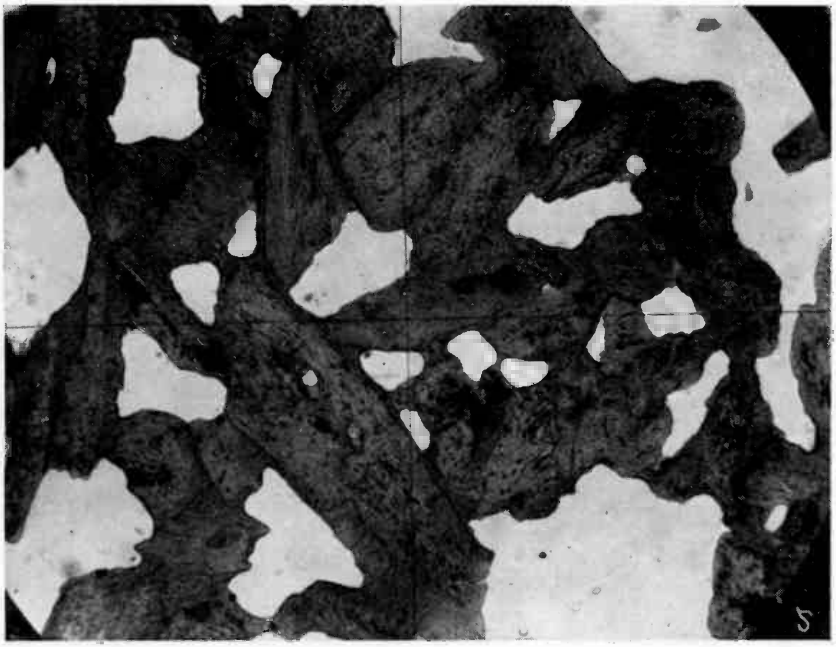

Plate II.—Steamed bone meal, 40-60 mesh, alkali-acid treated.

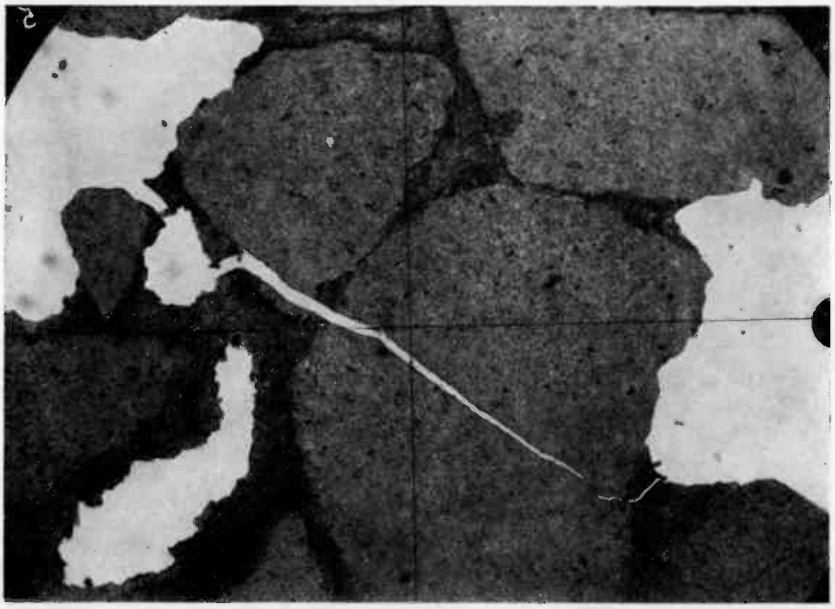

Plate III.—Defluorite, synthetic tricalcium phosphate, 20-40 mesh.

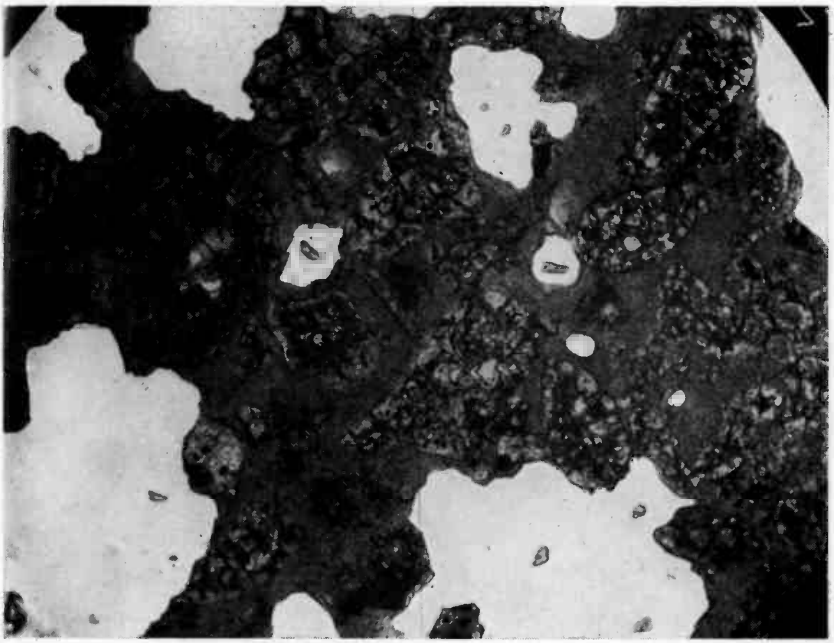

Plate IV.—Rock phosphate, untreated.

The porosity of the bone and Defluorite is evident from the pictures, perhaps explaining in some measure the greater fluoride-removing power of these two materials over that of the rock phosphate.

MECHANISM OF THE REACTION

When the work on bone was first begun in 1934 at the University of Arizona by H. V. Smith, the formula of bone was considered to be $[Ca_3(PO_4)_2]n \cdot CaCO_3$ where n was 2 or 3. It was assumed that the sodium hydroxide treatment resulted first in the formation of a hydroxy-apatite; that the following hydrochloric acid formed the chlorapatite; and finally that the fluorine of the water displaced the chloride radical with the formation of a fluorapatite, thus removing the fluorine from the water. The possibility of anion exchange was first suggested by Gassmann (12). The following series of equations may help to show the supposed reactions.

$$[Ca_3(PO_4)_2]n \cdot CaCO_3 + 2NaOH \rightarrow [Ca_3(PO_4)_2]n \cdot Ca(OH)_2 + Na_2CO_3$$
$$[Ca_3(PO_4)_2]n \cdot Ca(OH)_2 + 2HCl \rightarrow [Ca_3(PO_4)_2]n \cdot CaCl_2 + 2H_2O$$
$$[Ca_3(PO_4)_2]n \cdot CaCl_2 + NaF \rightarrow [Ca_3(PO_4)_2]n \cdot CaF_2 + 2NaCl$$

This assumption may not be true for several reasons—namely, (1) the amount of fluorine taken up by the bone from the water does not approach the theoretical value assuming a complete conversion of the chlorapatite to the fluorapatite, but since the reaction may only be a surface phenomenon, this reason may not be important; (2) the chloride content of the bone after treatment with HCl has been found by analysis to be less than 0.19 per cent chloride, indicating that the second step is only partial; (3) assuming the reaction of anion exchange, it should be possible to regenerate the bone with high concentrations of NaCl, but this has been found impossible; (4) regeneration of the bone can be accomplished with a number of acids, including organic acids, which indicates that the formation of a chlorapatite is not necessary for the success of the removal but that the acid serves possibly only to neutralize the excess alkalinity; and (5) no evidence of a true chemical reaction (anion exchange exclusively) is found when an adsorption isotherm is determined for the bone and the fluorine.

The true mechanism of the reaction is still in a conjectural stage. An adsorption isotherm for the reaction was determined by use of the well-known Freundlich equation. Results of this experiment indicate that the mechanism is neither true chemical reaction nor is it adsorption alone.

The Freundlich equation is as follows:

$$x/m = KC^{1/p}$$

where x is the grams of material adsorbed (fluorine)
m is the grams of adsorbing material (bone)
C is the equilibrium concentration with respect to the adsorbed ion (fluorine)
K and $^1/_p$ are constants for each particular system

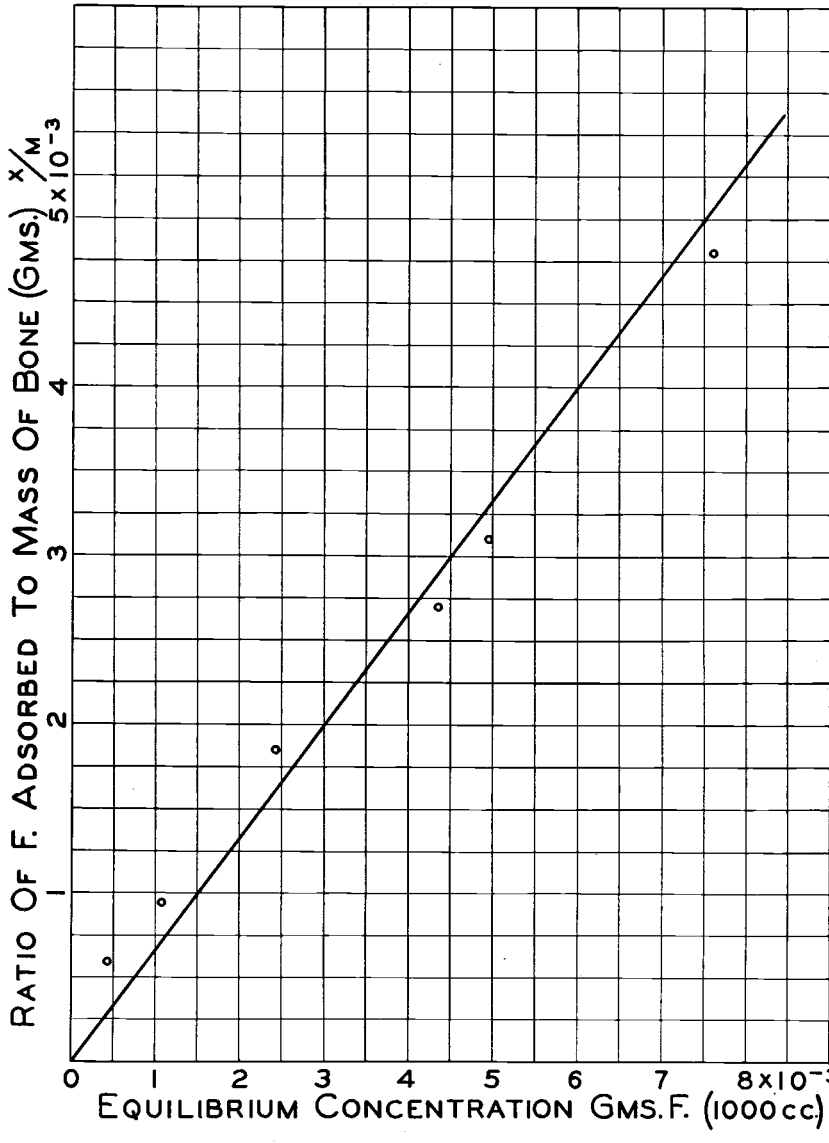

Figure 5.—Freundlich isotherm curve for bone-fluorine equilibria.

The details of the study were as follows: Samples of activated bone, weighing 2 grams, were shaken several days (equilibrium) in glass stoppered bottles with fluorine solutions ranging in concentration from 0 to 30 p.p.m.; the mixtures were filtered, and the residual fluorine of the solution (C) determined in each case by titration with standard thorium nitrate solution using the

Rowley and Churchill modification of the Willard and Winter method. The ratio x/m was plotted against C (Fig. 5). According to Freundlich, the curve for a true adsorption process is exponential, and for a simple chemical reaction the curve obtained parallels the C axis. However, the curve obtained in this study is seen to be a straight line of positive slope indicating the formation of a solution of varying composition, which in this case would obviously be solid-solution formation. Other investigators have also noted this tendency toward solid-solution formation. Hendricks, Hill, Jacob, and Jefferson (14) in discussing the composition of bone and phosphate rock state that "it would be expected that carbonate apatite (bone) could form solid solutions with hydroxy fluor-, oxy-, or possibly sulphate apatite. Many of the minerals mentioned in the first part of the article are members of such solid solutions." This then might possibly be the mechanism. It is conceivable that the treatment of the bone with sodium hydroxide might cause a partial conversion to the hydroxy-apatite. The hydroxy-apatite thus formed might react with fluorine of the water to form a certain amount of hydroxy-fluorapatite, which according to Hendricks, might be expected to form solid solutions with carbonate apatite (bone). Removal of fluorides from water would thus be effected. The acid treatment would serve merely to neutralize the excess alkali, since it has been shown that the removal takes place best at a *p*H below 8. That any displacement which occurs involves the hydroxyl or carbonate group rather than the chloride radical is substantiated by the *p*H measurements shown in Table 19. It is noted that the *p*H of the reacting mixture increases with time of contact of the bone with the water. Since the amount of fluorine removal increases with the time of contact, it is very probable that the increase in *p*H noted is due to the partial displacement of either the hydroxyl or carbonate group. After this partial reaction, solid solutions may be formed.

PRACTICAL APPLICATIONS

The practicability of the use of bone for removing fluorine from drinking water has been demonstrated by a number of laboratory and field studies. Two types of filter have been designed for home and school use—the olla filter and the pressure filter.

The olla filter consists of an unglazed earthen jar (olla cooler) drinking fountain (Pl. V). These coolers are common equipment in offices and homes. A charge of bone is put into a 3×11-inch cylinder which is then closed top and bottom by means of fine mesh brass screens. The cylinder is placed in the olla and a 5 gallon bottle of water set in place on top of the cooler. The apparatus is so designed that the neck of the bottle fits an inch or 2 into the cylinder in such a way that the water must filter down through the bone and out the bottom of the cylinder. Percolation continues until the water level outside in the olla becomes the same as that in the cylinder. Water may then be drawn off at will from the tap. When water is removed by means of the tap,

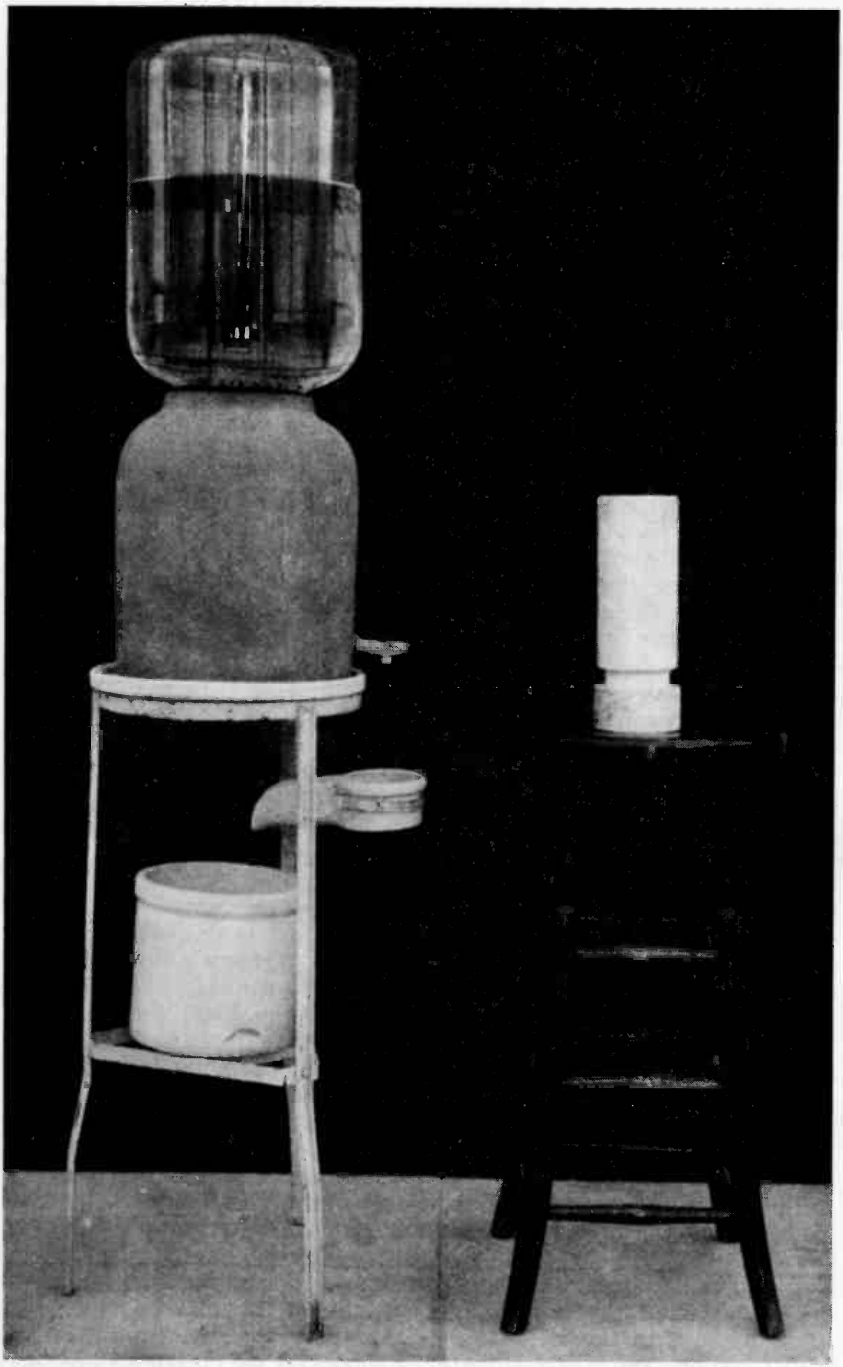

Plate V.—Olla type cooler drinking fountain showing cartridge at right.

more water from the bottle percolates down through the bone in the cylinder until equilibrium is again established between the two water levels. In this manner a reserve supply of treated water becomes available for use.

Several studies were conducted on this type of filter with good results. The first of such a study involved the use of a cartridge of bone containing 1.59 pounds of bone. The cylinder in this case consisted of a 3 × 11-inch transit pipe which was filled to a depth of about 9 inches with 40-60 mesh bone and then sealed in by means of the brass screens. Water containing 3.5 p.p.m. of fluorine was passed through the bone as rapidly as possible. Samples were taken after the passage of every 5 gallons and analyzed for fluorine by the Sanchis method. A total volume of 165 gallons of the water was defluorinated by the 1.59 pounds of bone before the toxic level of 0.9 p.p.m. of fluorine was reached. This corresponds to the removal of 1.37 grams of fluorine per pound of bone or 67.13 grams per cubic foot of bone. Results of the study are shown in Table 25.

TABLE 25.—REMOVAL OF FLUORINE WITH THE OLLA TYPE FILTER (40-60 MESH BONE).

Weight of bone in cartridge (pounds)	Volume of water treated (gallons)	Fluorine content (p.p.m.)
1.590	0 (control)	3.50
	50	0.00
	100	0.00
	150	0.00
	155	0.10
	160	0.35
	165	0.75
	170	1.20
1.799	0 (control)	11.00
	25	0.00
	50	0.00
	55	0.00
	60	0.50
	65	1.50

The second study involving the olla filter consisted in the use of a cartridge of bone containing 1.799 pounds of bone through which was passed a water containing 11 p.p.m. of fluorine. This cartridge of bone treated 60 gallons of water which corresponds to a removal of 1.43 grams of fluorine per pound of bone or 70.1 grams per cubic foot of bone. It is of interest to note that the total amount of fluorine removed per cubic foot of bone is the same regardless of the initial concentration of the fluorine. Results of this study are also shown in Table 25.

The second type of filter designed—namely, the pressure filter, is more applicable to those situations in which a large quantity of water is needed in a short time. This type of filter is best adapted

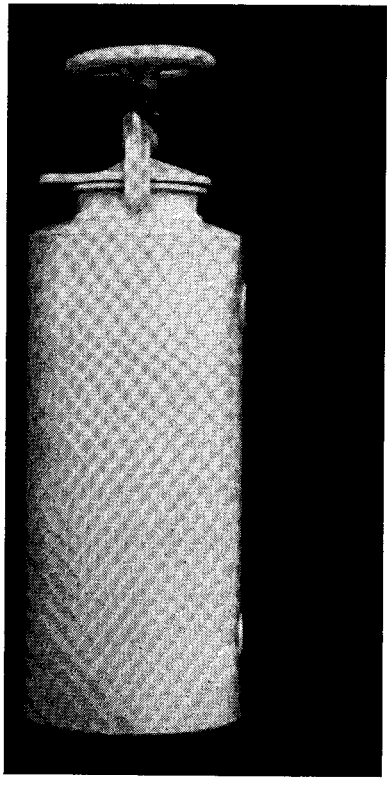

Plate VI.—Pressure type filter.

for general domestic use including cooking and drinking and for use in schools. The unit consists of a closed cylinder with an inlet for the water at the top and an outlet at the bottom (Pl. VI). The opening is designed to produce a spray effect when the water is passed in order to prevent channeling. The bottom outlet is covered with a fine-mesh screen to prevent loss of the bone. The size of the cylinder depends upon the initial fluoride content of the water and the demands made upon it. In most of the work carried out in the field a 10- to 12-pound unit was used.

A number of field trials have been conducted throughout the state with this pressure type filter. The most extensive, however, were those carried on at the Pima County Preventorium, an institution organized for the purpose of building up children suspected of having tuberculosis or who have been in contact with the disease. The age of the children varies from about eight to fifteen years, just the age at which mottled enamel is most likely to occur. When it was found in May, 1938, that the water used by the children (130 in all) was toxic, containing 4.0 p.p.m. of fluorine, it was suggested that these bone filters be installed. Since that time these pressure units have been supplied. Daily samples of the effluent water were taken by the attendant at the Preventorium and sent to the laboratory for analysis. In this way a closely controlled series of field experi-

TABLE 26.—REMOVAL OF FLUORINE WITH BONE (40-60 MESH) IN THE PRESSURE FILTER AT THE ORACLE PREVENTORIUM.

Volume passed (gallons)	Fluoride content (p.p.m.)
Control	4.0
90	0.5
450	0.0
835	0.0
888	0.75
968	0.80

ments was conducted. Results of one of the thirty-six trials so far conducted by a pressure unit containing 11 pounds of bone are shown in Table 26.

It is seen that the bone removed a total of 14.5 grams of fluorine in treating the 968 gallons of 4.0 p.p.m. fluorine water. This corresponds to a removal of 1.32 grams of fluorine per pound of bone or 64.7 grams per cubic foot of bone.

REMOVAL OF FLUORINE FROM CIDER

During recent years it has become the practice to spray fruits and vegetables with fluorine sprays. This procedure is particularly prevalent in the Pacific Northwest. First-grade apples can bear the cost of fluorine removal by washing, but the cost of cleaning second-grade fruit and culls which are used for making cider is not justified economically. Therefore, much of the cider produced in this region carries high concentrations of fluorine. The removal of this element presents a serious problem to the orchardist. The successful use of bone for the removal of fluorine from drinking water suggested the possibility of using this same treatment on cider containing high concentrations of fluoride.

The first study conducted on this problem consisted of the preparation of standard fluorine-cider solutions by adding standard sodium fluoride to the cider. These solutions were then shaken for 1 hour in an end-over-end shaker with different amounts of bone and the residual fluorine content then determined. The method of analysis for fluorine becomes quite complex when organic matter is present, such as in the case of cider. Under these conditions a preliminary 16 to 24-hour ashing with especially pure calcium hydroxide is needed. The fluorine content is then determined by distillation of the ash under the Willard and Winter procedure. Results of this study are shown in Table 27.

TABLE 27.—REMOVAL OF FLUORINE FROM CIDER BY SHAKING WITH BONE.

	Weight of bone (grams)	F content (p.p.m.)
Original cider	0	0.72
242.5 cc. cider plus 7.5 cc. of 100 p.p.m. solution of fluorine gives approximately 3 p.p.m. F	1	0.37
247.5 cc. cider plus 2.5 cc. of 1,000 p.p.m. solution of F gives approximately 10 p.p.m. F	5	0.56

It is seen that the cider used did contain some fluorine and that the additional fluorine added was removed by shaking with the bone.

The second study conducted on this problem consisted in passing a 10 p.p.m. fluorine-cider solution through a column of 100 grams of bone in a glass tube whose diameter was 2.2 centimeters. The bone used was 40-60 mesh calcined bone. Samples were taken at

the end of the passage of every 200 cc. and analyzed for the fluoride content by ashing and distilling as explained above. Results are shown in Table 28.

TABLE 28.—REMOVAL OF FLUORINE FROM CIDER BY A COLUMN OF BONE (40-60 MESH CALCINED).

Sample	Initial F (p.p.m.)	Residual F (p.p.m.)
First 200 cc.	10	0.32
Second 200 cc.	10	0.15
Third 200 cc.	10	0.33
Fourth 200 cc.	10	0.10
Fifth 200 cc.	10	0.28
Sixth 200 cc.	10	0.20

FLUORINE REMOVAL BY OTHER PHOSPHATES

A number of materials which were either similar to bone or which it was thought might have possibilities for use in fluorine removal were investigated. Most of these studies involved shaking the material with a standard fluorine solution and noting the residual fluorine content of the filtrate. None of the materials tried showed any marked fluoride-removing power with the exception of bone black; but five times as much of this material was necessary to effect the same removal as in the case of activated bone. The standard potency test was conducted on these other phosphates using in some cases 10 grams of the material instead of the usual 2 grams used in the test. Results of this study are shown in Table 29.

TABLE 29.—FLUORIDE-REMOVING POWER OF OTHER PHOSPHATES.

Material and treatment	Weight of material used (grams)	Residual fluorine (p.p.m.)
Aluminum phosphate (powder—not treated)	2	1.0
Ferric phosphate (powder—not treated)	2	2.2
Florida rock phosphate (raw rock—alkali and acid treated)	2	2.6
Florida rock phosphate (calcined rock—alkali and acid treated)	2	1.75
Jacobs rock phosphate (calcined at 1,400° C.)	2	2.3
Jacobs rock phosphate (alkali-acid treated)	10	1.5
Bone black (untreated)	2	1.5
Bone black (alkali-acid treated)	10	0.6
$Ca_3(PO_4)_2$ and CaCO mixture, 300 gm. and 50 gm.	2	1.25
Powdered eggshell (alkali-acid treated)	2	1.75
Calcined bone (alkali-acid treated, calcined, acid treated)	2	0.57

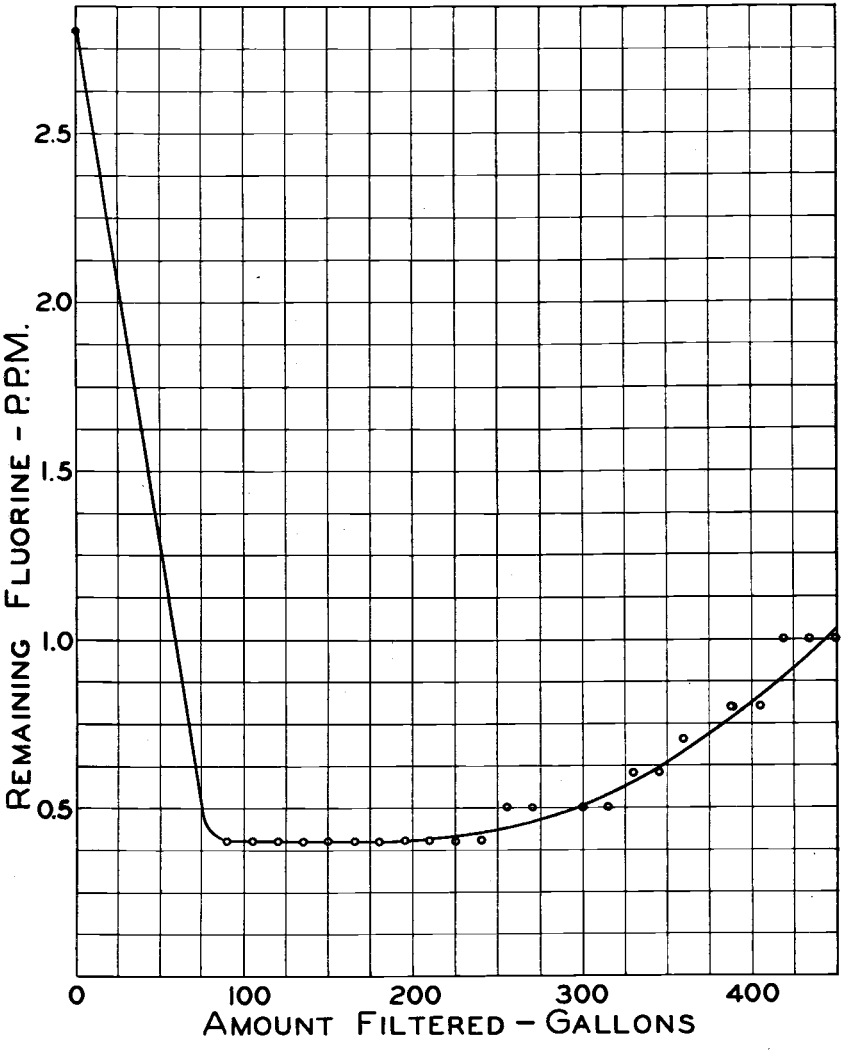

Figure 6.—Removal of fluorine from water—St. David School.

Other tests included the precipitation of tricalcium phosphate from solutions containing fluorine as suggested by MacIntire (18). This study involves mixing phosphoric acid, calcium hydroxide, and clay and allowing the precipitate formed to settle out. According to MacIntire, good removal should result, but the experiment proved a failure when tried at Arizona. Results of the study are shown in Table 30.

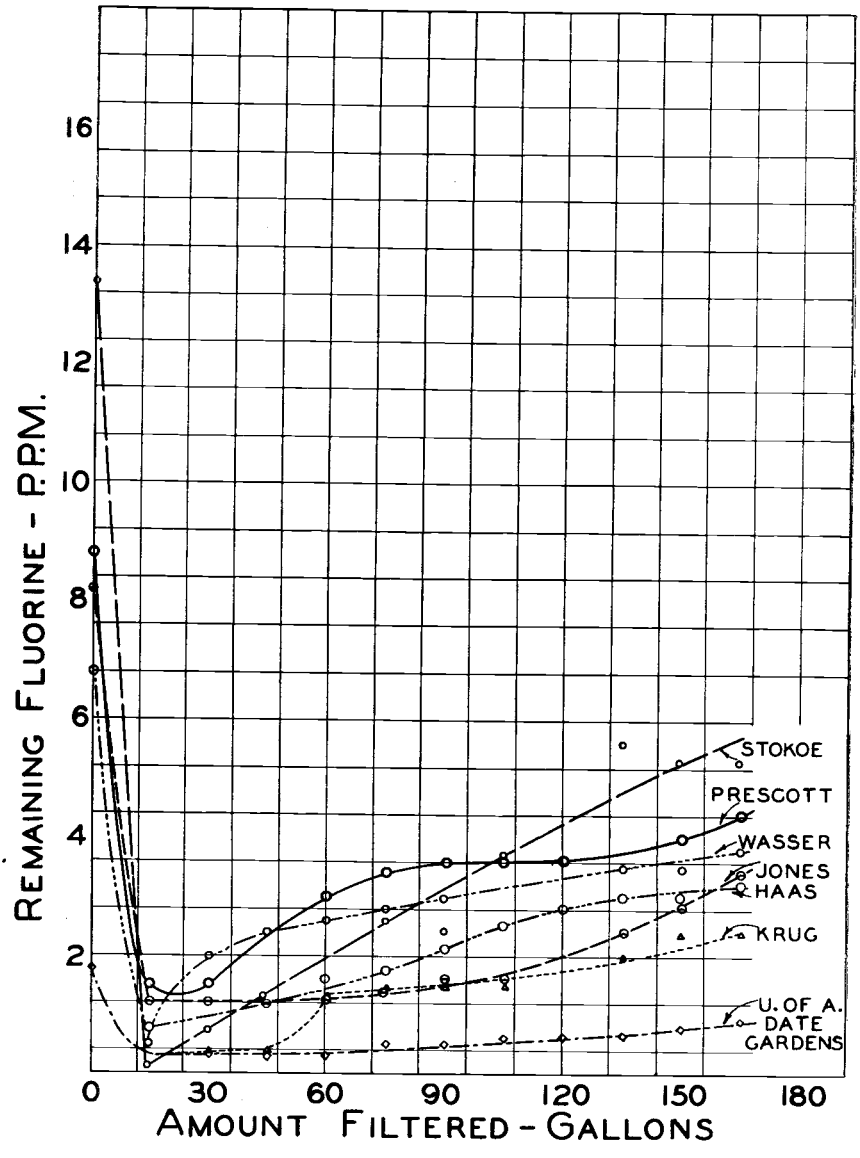

Figure 7.—Removal of fluorine from water using activated alumina.

Field experiments using Defluorite (synthetic tricalcium phosphate) furnished by the National Aluminate Corporation were conducted by E. O. Foster, Assistant Chemist in the Arizona Agricultural Experiment Station branch laboratory at Phoenix, Arizona. While good results were obtained using this material

TABLE 30.—REMOVAL OF FLUORINE BY THE PRECIPITATION METHOD.

Initial fluorine (p.p.m.)	Suspended matter added (p.p.m.)	Calcium hydroxide added (p.p.m.)	Phosphoric acid added (p.p.m.)	Residual fluorine (p.p.m.)
6.0	250	271	190	6.0

it was found that activated bone which is heavier and harder than the synthetic product was almost twice as effective per unit of volume in removing fluorine from water.

A number of field studies were conducted throughout the state with activated alumina furnished also by the National Aluminate Corporation. This substance was also known as Defluorite at one time. The material was not found to function in the removal of fluorides to any marked degree. Results of these studies are shown in Figures 6 and 7.

GENERAL DISCUSSION

The effectiveness of the use of bone in removing fluorine from water has been investigated. It has been found that bone will reduce the fluoride content but that the degree of removal is dependent on a number of factors, especially the fineness of subdivision of the bone and the time of contact of the bone and water. Probably the most important consideration is the preparation and activation of the bone itself. The experiments which have been conducted show that the best bone product from an all-around point of view is the 40-60 mesh bone prepared by the calcination process which has been described. This bone shows not only the greatest fluoride-removing power, but it has a number of other advantages as well, including less loss by attrition, greater ease of wetting, and no tendency to putrefy.

The two types of filters which have been developed have been designed to give the maximum amount of fluorine removal with the least possible effort on the part of the user. The olla filter has been designed mainly for the treatment of drinking water. This type of unit is simple in operation, low in expense, and at the same time very convenient for home and office use. The cartridges of bone can be easily and quickly changed whenever the capacity of the bone has been reached. The necessity for strict control, however, in the operation of these filters cannot be overemphasized. The amount of bone to be used in any case is a function of the fluoride content of the water, the rate of flow, and volume of water needed. For every new unit installed, the size of the filter should be correlated with the above-mentioned conditions.

In the field work which was conducted at the Pima County Preventorium, strict control was maintained by taking water samples each day and analyzing for the fluoride content. Whenever the

effluent water reached a value of 0.9 p.p.m. of fluorine, the toxic level, a fresh charge of bone was installed. Similar control should be exhibited over the filters used by the individual.

In the case of the operation of the olla filter, it is suggested that a small test kit be included with the unit so that tests could be made by the user from time to time. This test kit contains two 100 cc. Nessler tubes, a 5 cc. pipette, a bottle of acid-indicator mixture, and a large bottle of a 1 p.p.m. fluorine solution. This is sufficient equipment to make a field test using the Sanchis method as modified by Scott[1] who has shown that the acids and the indicator solution may be combined and that boiling is not necessary for the production of the color. The test involves the following steps: (1) one Nessler tube should be filled with the effluent water and the other tube with the standard 1 p.p.m. fluorine solution; (2) 5 cc. of the acid-indicator[2] mixture should be added to each tube by means of the pipette; (3) the solutions should stand for 1 hour and the resulting colors be compared. A comparison of the effluent water with the standard shows the user the status of the bone in the filter. If the color of the water is pinker than the standard, the capacity of the bone has not been reached; however, if the color is yellower than the standard, the bone has become exhausted and a fresh charge or cartridge should be installed. A record kept of the number of gallons used indicates the time to change the bone in future cases.

It is estimated that these olla type filters including cooler and cartridge of bone could be placed on the market for about $15 to $20. Since it is known that the capacity of the bone will eventually be reached, a service must be maintained to supply fresh bone and to regenerate the spent bone.

The size of the cartridge used in the olla filter in the laboratory studies limited the amount of bone which could be incorporated to about 1½ pounds. Larger cartridges and even larger coolers could be constructed such that the amount of water on reserve could be increased as well as the total volume of water treated per charge of bone.

The pressure type of filter has been designed for more rigorous use. This unit is best adapted to those conditions in which a large supply of water is needed in a short time. Here again, however, the amount of bone to be used is dependent on the initial fluoride content of the water, the rate of flow, and the volume of water needed. For general all-around domestic use including cooking as well as drinking, this type of filter is recommended.

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[1] Unpublished results.

[2] Dissolve 1 gram of zirconium nitrate in 100 cc. distilled water and 0.2 gram of alizarin red S in 100 cc. distilled water and mix the solutions. Prepare 1 liter of 2.6*N* hydrochloric and sulphuric acids and mix. Transfer 70 cc. of zirconium-alizarin mixture to a 1-liter flask and make up to 1,000 cc. with the mixed acid solution. Use 5 cc. of this acid indicator per determination.

This indicator solution must be kept cold to prevent separation of the indicator from the acid.

The size of the filter can be increased to fit the requirements placed upon it. A rather large filter, for example, would undoubtedly be required for use in a school where the consumption of water is, at intervals (play periods, etc.), rather rapid.

It has been shown that the length of life of the bone is increased by longer time of contact, which, in this case, would mean a slower flow rate. The capacity for fluoride removal of one of these types of filters could be increased by the construction and use of a reservoir tank. Water could be then passed through the filter at a reduced rate of flow into the tank thus building up a large supply of treated water and, at the same time, increasing the length of life of the bone and the effectiveness of removal. A flow rate of 25 to 30 gallons or less per hour is recommended on a 10-pound unit, because greater flow rates do not effect as good a removal, and the capacity of the bone becomes exhausted more quickly.

Since these units are placed directly in the water line, the necessity for control becomes greater than ever. For each new unit installed the amount of bone necessary should be correlated with the initial fluorine content of the water, the rate of flow desired, and the volume of water that is expected to be used per unit of time. Each filter should be equipped with a meter fitted with an automatic alarm to indicate that regeneration of the bone is necessary. The standard test kit previously described should be supplied with these units. After the bone has become exhausted, fresh charges should be installed. It is possible to regenerate the bone in the home but more practical to exchange the unit for a fresh one.

A number of field and laboratory tests have shown the practicability of the use of bone in the removal of fluorine from water. The cost of production of these units cannot as yet be determined, but the cost of bone, chemicals, calcination, labor, and overhead must all enter into the final price.

The practicability of the use of bone on a municipal scale has not as yet been determined, but little reason is seen to prohibit its use. From a study of flow rates it can be shown that the size of the filter bed necessary for the passage of 1,000,000 gallons of water per 24 hours per 12-inch depth of bone is 10 square feet in the case of 10-20 mesh bone, 60 square feet for 20-40 mesh, and 100 square feet for 40-60 mesh. Consider the application of the use of bone for fluorine removal in the case of a city using 1,000,000 gallons of water per day containing 3.5 p.p.m. of fluorine. It has been shown that 1 cubic foot of bone (40-60 mesh) will treat 4,900 gallons of a water containing 3.5 p.p.m. of fluorine. The amount of bone necessary, therefore, to treat the 1,000,000 gallons of water is given by the ratio 1,000,000/4,900 which is 208 cubic feet. The filter bed required for treatment of this water using 40-60 mesh bone would have to be at least 10 feet square and 2 feet deep, which is not beyond the realm of possibility considering that bone can be reactivated. If the depth of the filter bed is increased its area can be decreased, thus filtration by means of pressure may become necessary.

SUMMARY AND CONCLUSIONS

1. The Sanchis method for the determination of fluorine in water was investigated and found to be affected by several ions. The phosphate ion causes low results, and the sulphate ion causes high results with this method.

2. Bone may be prepared for use in removing fluorine from water by boiling with alkali till the material has lost its flinty characteristics and has become snow white in appearance, washing out the excess alkali with water, and neutralizing with a dilute hydrochloric acid treatment.

3. After use of the bone for the fluoride-removal process, it can be regenerated for further use by again treating with alkali and acid. An overnight treatment of the bone with cold alkali (0.25*N*) followed by a 10-minute wash with a dilute acid, such as acetic or hydrochloric acid (0.10*N*), is recommended since less solubility loss occurs.

4. Calcination of the bone at 400 to 600 degrees C. for 10 minutes followed by a 10-minute acid treatment yields a better bone product for the fluoride-removal process. Bone prepared in this manner will not putrefy as do some of the alkali-acid activated products.

5. The effect of mesh was investigated and was found to play an important part in the process of removal, the finer fractions removing the greater amount of fluorine. A 40-60 mesh has been found most desirable.

6. The time of contact of the bone and the water has been found to be of considerable importance, more fluorine being removed on the greater time of contact.

7. The *p*H of the water has little effect on the amount of fluorine removed by bone over a range of *p*H 3 to 8. At higher *p*H values the removal is decreased, but since few domestic waters ever attain any such degree of alkalinity, the effect is considered insignificant.

8. Temperature has been found to have no effect on the fluoride-removing power of bone.

9. The effect of the presence of salts other than fluorine in waters on the amount of fluorine removed by bone was investigated and was found to have only a very slight effect, tending in some cases to decrease the amount of fluorine removed.

10. Double treatment of water with two portions of bone was found to function no better than a single treatment with twice as much bone.

11. The mechanism by which bone removes fluorine from water appears to be through the formation of solid solutions rather than simple anion exchange as was first supposed.

12. Fluorine removal by other phosphates has been investigated, but none has functioned as well as bone. The synthetic tricalcium phosphate product of the National Aluminate Corporation known as Defluorite was found to possess the capacity for

fluorine removal, but on the volume basis bone has been shown to be about twice as effective.

13. The practicability of the use of bone for removing fluorides from drinking water has been demonstrated by a number of field and laboratory studies.

14. Two types of filters for domestic use, the olla and pressure filters, have been presented and their practicability proved by a number of field studies.

15. The bone method presented appears to be the most practical and economical method that has as yet been devised for removing fluorine from drinking water.

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