THE REMOVAL OF FLUORIDES FROM PUBLIC WATER SUPPLIES

THESIS

THE REMOVAL OF FLUORIDES FROM PUBLIC WATER SUPPLIES

THESIS

**Presented to the faculty of the Graduate Division
of the Texas Technological College in Partial
Fulfillment of the Requirements**

For the Degree of

MASTER OF SCIENCE

By

James Barron Litton, B. S.

Lubbock, Texas

August, 1940

AC
805
T3
1340
no. 22
cap. 2

ACKNOWLEDGMENTS

I wish to express my appreciation to the International Filter Company for making this work possible through the use of their equipment, to Mr. H. F. Martin of that company for his helpful suggestions throughout the test, and to the members of the Advisory Committee for their help in the writing of this thesis. I am especially grateful to Dr. R. C. Goodwin, under whose supervision this work was done.

TABLE OF CONTENTS

CHAPTER	PAGE
I. Introduction	1
II. Previous Removal Methods	5
III. Methods of Analysis	7
IV. Equipment	10
A. Pilot Plant Fluorex Purifier	10
B. Home Purifier	13
V. Experimental Procedures and Results	15
A. Water Supply Tested	15
B. Pilot Plant Purifier	21
Rated Capacity	21
Actual Capacity	23
Effect of Flow Rate on Capacity	29
Effect of Alkali Used Per Regeneration on Capacity	32
Fluoride Content of Regeneration Wash Waters	32
Loss of Fluorex	34
Cost of Operation of Unit	35
C. Home Purifier	40
D. Fluosilicate Determinations	41
VI. Conclusions	44
Bibliography	46

CHAPTER I

INTRODUCTION

The disease now known as chronic endemic dental fluorosis or mottled enamel was first recorded by Eager in 1901¹ and rediscovered in 1916 by Black with the collaboration of McKay.² Some of the earlier theories placed the cause of mottled enamel on the presence of iron and manganese in the water while others suggested that various diet deficiencies, such as the lack of calcium, might cause the stain. However, the disease was traced to underground water supplies by McKay in 1926.³

In 1931, Smith, Lantz and Smith⁴ and Churchill⁵ showed that fluorides in the water supply caused mottling of the enamel. Their work was immediately followed by investigations on the distribution of endemic areas, the analysis of fluorides, the relative toxicity of the fluorine compounds and the study of suitable methods for the removal of the harmful ion from drinking water.

Endemic areas are found in most every part of the world, and the United States has about 360 known or reported affected areas of which 27 per cent are in

Texas. The West Texas-Panhandle region is the largest affected territory in the United States and is probably the largest in the world. The map on page 3, which was compiled by the Texas State Department of Health, shows how widespread are the affected areas over the state. The fluoride content of the water supplies is also indicated.

H. Trendly Dean, in a summary of the extent of mottled enamel in Texas,⁶ showed that a definite quantitative relation exists between the fluoride concentration of the water supply and the extent of fluoroses. With reference to the concentrations necessary to produce mottling, he writes: "If a water containing about one part per million is used continuously for both drinking and cooking during the period of permanent tooth calcification, it is likely that the very mildest forms of mottled enamel may develop in about 10 per cent of the group. In waters containing about 1.7 or 1.8 parts per million the incidence may be expected to rise to 40 or 50 per cent, but in practically all cases being of the 'very mild' or 'mild' type. Around 2.5 parts per million the incidence may rise to 75 or 80 per cent. At 4.0 parts per million the incidence is generally in the neighborhood of 90 per cent. In concentrations of 6.0 parts per million or higher, an incidence close to 100 per cent is not unusual." The period of permanent tooth calcification occurs during the first 8 years of

a child's life. The safe limit is now considered to be 1.0 part per million.

Although the case of fluorosis on dental structure has been proved, recent investigations have indicated that the presence of fluorides in drinking water might be a blessing in disguise. Children living in endemic areas, even though affected with mottled enamel, have shown a limited immunity from dental caries. Some evidence has^{7,8,9,10,11} been given to support this theory. Cox has¹² made a report on the latest developments of this theory. However, the fact remains that dental fluorosis is still a serious problem. As far as children's teeth are concerned, the evidence seems to show that the disadvantages of mottled enamel outweigh any advantage that might result through the use of fluoride contaminated water.

Since fluorides in the water do have a deleterious effect on the structural formation of the permanent teeth and in addition decrease their esthetic value, some practical method of fluoride removal should be available to a community where a non-contaminated source of water is not obtainable. Lubbock, Texas, is a good example of a community having just that problem. This investigation was undertaken to determine whether a process developed by the International Filter Company could be adapted to the needs of this community for the economical, large-scale removal of fluorides from the public water supply.

a child's life. The safe limit is now considered to be 1.0 part per million.

Although the case of fluorosis on dental structure has been proved, recent investigations have indicated that the presence of fluorides in drinking water might be a blessing in disguise. Children living in endemic areas, even though affected with mottled enamel, have shown a limited immunity from dental caries. Some evidence has^{7,8,9,10,11} been given to support this theory. Cox has¹² made a report on the latest developments of this theory. However, the fact remains that dental fluorosis is still a serious problem. As far as children's teeth are concerned, the evidence seems to show that the disadvantages of mottled enamel outweigh any advantage that might result through the use of fluoride contaminated water.

Since fluorides in the water do have a deleterious effect on the structural formation of the permanent teeth and in addition decrease their esthetic value, some practical method of fluoride removal should be available to a community where a non-contaminated source of water is not obtainable. Lubbock, Texas, is a good example of a community having just that problem. This investigation was undertaken to determine whether a process developed by the International Filter Company could be adapted to the needs of this community for the economical, large-scale removal of fluorines from the public water supply.

¹⁷
 Stewart worked on the reduction and removal of fluorides from Lubbock water with some success. His investigations included alum, lime softening, sodium hydroxide and defluorite.

The removal of fluorides by tricalcium phosphate, now known as fluorex, was investigated in 1937. Adler, Klein and Lindsay¹⁸ used the synthetic material in a contact filter. They found that regeneration of the exhausted material with sodium hydroxide followed by a water and hydrochloric acid wash was possible. Each regeneration resulted in the loss of 2.5 to 3 per cent of the material. Smith and Smith¹⁹ used prepared crushed bone²⁰ successfully. Behrman and Gustafson of the International Filter Company found that the use of hydrochloric acid resulted in the loss of the material with each regeneration and also that the bulk density of the material was greatly increased. After 25 regenerations, the activity of the material was found to be practically zero. In an improved method of regeneration, carbon dioxide gas was used to neutralize the excess sodium hydroxide instead of hydrochloric acid. The use of this method seemed to eliminate all of the disadvantages of the older method. They found that after 200 regenerations the original volume of the material was undiminished, the fluoride removal capacity was constant, the density was the same as before, and the porosity and particle size of the granules were preserved.

CHAPTER III

METHODS OF ANALYSIS

After fluorine was found to be the causative factor in the mottling of enamel, investigations were started on methods of analysis which would be more accurate and less difficult than the older methods.

One of the most widely accepted methods at the present is that of Sanchis.²¹ This method was used in this investigation because it is dependable and adaptable to procedures that require the determination of several dozen samples at the same time. Since the fluoride concentration of the water used in this investigation was about 4.7 parts per million, the procedure used by Sanchis had to be altered slightly when testing the tap water. The concentration of the zirconium-alizarin indicator was doubled; thus all of the reddish color was not bleached out of the sample. In this way comparisons were easier and more accurate than diluting each sample. For determinations below 3 parts per million, the procedure was not altered. A fresh solution of the indicator was prepared every week. To eliminate one operation in the procedure, the 3N HCl and H_2SO_4 were prepared by mixing equal volumes of the 6N acids.

Another method used was that of the Texas State Department of Health. In this procedure the sulphates were first precipitated in an acid solution by barium chloride. The solution was allowed to stand for 48 hours before decanting the sample from the barium sulphate. The sample was then compared colorimetrically using a zirconium-alazirin indicator. The writer found that the use of a centrifuge was quicker and that decantation was easier since the precipitate was not disturbed.

During these determinations six standards were used. Both sodium and lithium fluoride were tried, and essentially the same results were obtained from the use of either standard.

In order to get a more accurate determination on the fluoride in the water supply, as well as find the fluoride content of the regeneration wash waters, the Boruff and Abbott²² method was used. Their procedure²³ was a modification of the Willard and Winter method. The fluoride in the sample was first distilled as fluosilicic acid, and the acid subsequently titrated against a standard thorium nitrate solution. The²⁴ alazirin indicator suggested by Armstrong²⁴ was found to be the most accurate.

Phosphates were determined colorimetrically by the method of Faber and Young²⁵. Later experiments were made in an effort to determine whether the

fluosilicate ion existed in the tap water. Silica determinations were made colorimetrically using the method of Schwartz.²⁶ A permanent standard was made from potassium chromate buffered with sodium tetraborate. A titration method was attempted for determining fluoride and fluosilicate ions. The procedure used by Geffcken²⁷ and Hamann was modified using very dilute solutions; however, satisfactory results were not obtained.

CHAPTER IV

EQUIPMENT

A. Pilot Plant Fluorex Purifier

The pilot plant used in this field test was made by the International Filter Company in order to test its effectiveness on natural water supplies. On page 11 is the elevation and plan view of the equipment layout. The picture on page 12 shows the plant after being set up ready for service.

The two main operations of the unit were regeneration and purification. Regeneration took place in the following steps: backwash, alkali delivery, downward rinse, and neutralization. To backwash the unit, valve 4 was opened wide and the flow rate was adjusted to 5-1/2 gallons per minute by valve 3. After the waste water became clear, valves 3 and 4 were closed. This operation usually required 2 to 3 minutes.

The sodium hydroxide delivery was carried out as follows. 1.4 pounds of flake commercial alkali were dissolved in the caustic tank with water added up to 3-1/2 inches from the bottom. Valves 5, 6, and 9 were opened wide and valve 8 was adjusted so that the pressure gauge read 10 pounds. Cock 7 was adjusted before to

deliver the solution in 15 minutes. The 7 per cent solution in the caustic tank was diluted by the ejector supply water to a one per cent solution. When the alkali delivery was finished, valve 8 was closed, and the downward rinse was continued for thirty minutes. Valves 9 and 6 were then closed.

To neutralize the excess alkali, valve 1 was adjusted to deliver 2-1/2 gallons of wash water per minute. The carbon dioxide gas tank shut-off valve and cock 11 were opened, and then regulator 10 was adjusted to read 23 pounds pressure. When the effluent was definitely acid to phenolphthalein indicator, cock 11, valve 5 and the CO₂ gas tank shut-off valve were closed. Neutralization usually required 20 to 30 minutes.

During the purification of the influent water, valve 1 was opened wide, and the flow rate was regulated by valve 2.

B. Home Purifier

The small home unit tested was made by the Red Jacket Manufacturing Company of Lavenport, Iowa. It was called the Red Jacket Portable Defluorite Unit #1L-1600.

The unit was 11 inches high and 8 inches in diameter. Four pounds of the tricalcium phosphate were placed between two metal screens, one 4 inches from the top, the other 8 inches from the top. Under the first screen was 1-1/2 inches of light gravel. An outlet was

at the bottom and side of the unit.

The operation of the unit consisted of first backwashing and then purifying. To backwash the unit, the effluent hose was attached to a faucet, and water was forced through the filter bed until the water coming out the top was clear. In order to meter the influent water, the large unit was used during the purification by the small filter. The large filter tank was first filled with water. Valve 3 was opened wide, and the flow rate was adjusted by valve 5. The water thus flowing from the waste line was introduced into the top of the small filter. A constant head of water was maintained throughout the run in the unit.

The water will flow normally at a rate of about 1 to 1-1/2 gallons per minute. However, the unit gave better service when a pinch clamp was put on the effluent line, and the flow rate was limited to about 0.5-0.8 gallons per minute. In order to eliminate packing, it was found that the filter should be backwashed after every 50 gallons of effluent.

CHAPTER V

EXPERIMENTAL PROCEDURES AND RESULTS

A. Water Supply Tested

The water used throughout this investigation was from the well on the campus of Texas Technological College in Lubbock, Texas. There is little difference in the city water supply and the school water. The water is rather hard and has an unusually high magnesium-calcium ratio.

A complete analysis was made of the well water by the International Filter Company. This analysis is given on page 16. According to this analysis, the fluoride content of the water was 5.2 parts per million. Although the fluoride content varies from time to time, the content is usually from 4.5 to 5.0 parts per million. Connell²⁸ analyzed this water in 1938 using the Fairchild method, and got about 4.2 ± 1 parts per million. Stewart used the Sanchis method in 1937, and found the fluoride content to be from 4.5 to 4.8 parts per million. During the present investigation the content varied to some extent, usually from 4.5 to 5.0 parts per million.

The following procedure was used in making the determinations by the Sanchis method, both for samples from the

purifier and the natural water supply. Standards were made having 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, and 3.0 parts per million of fluorides. The standards were found to be slightly cloudy if the ordinary distilled water was used, since the steam came through a long pipe line from the boiler before being condensed and, therefore, probably picked up some impurities.

Double distilled water was used throughout the entire test. Triple distilled water was found to be no more effective for the colorimetric procedures than was the double distilled water. 100 ml. of the samples were put in 250 ml. Erlenmeyer flasks. Each sample and standard was treated with 2 ml. of the 5N acid mixture and 2 ml. of the zirconium-alizarin lake reagent. Pipettes were used in adding the acid and indicator, since a small difference in the volume added was found to introduce an error. Burettes were quicker, but they were not used for the more accurate work.

Each sample and standard was brought quickly to boiling, and, after cooling for at least 4 hours, comparisons were made using 100 ml.essler tubes. Several dozen samples were usually determined at the same time.

Determinations made by the State Department of Health method were carried out as follows. For a fluoride content of less than 0.6 parts per million, 125 ml. of the sample were evaporated to 40 ml. after being treated with 1 ml. of 6N HCl. The cooled sample was then diluted

WATER ANALYSIS ON WELL WATER FROM TEXAS TECH-
NOLOGICAL COLLEGE BY INTERNATIONAL FILTER CO.

Determinations Made Hypothetical Combinations

Physical

	Parts Per Million		Parts Per Million
Suspended Matter	1.0	Calcium Carbonate	107
Turbidity	1.0	Magnesium Carbonate	137
Color	None	Magnesium Sulfate	88
Odor	None	Sodium Sulfate	116
		Sodium Chloride	147
Chemical			
Calcium (Ca)	43		
Magnesium (Mg)	57	Silica	60
Sodium (Na)	96	Total Dis- solved Solids	655
Alkalinity (as CO_3)	162		
Sulfate (SO_4)	149	Alkalinity (P) as CaCO_3	0
Chlorine (Cl)	89	Alkalinity (M) " "	270
Nitrate (NO_3)	n.d.	Total Hardness " "	343
Iron (Fe)	Trace	Calcium Hardness " "	107
Silica (SiO_2)	60	Magnesium Hardness " "	236
Fluorine (f)	5.2	Non-Carbonate Solids " "	201
Free CO_2	18	Total Solids " "	551
		Total Sodium Salts " "	205

pH 7.

to 55 ml., and 1 ml. of 6N HCl was added. The sulphates were precipitated by adding $\frac{1}{2}$ ml. of 6N HCl and 1 ml. of saturated BaCl_2 . If the sample contained from 0.6 to 3.0 parts per million of fluorides, only 55 ml. of the sample were used in the determination. The sulphates were precipitated as in the above case. For a fluoride content above 3 parts per million, samples containing 11 ml. and 27.5 ml each were diluted to 55 ml. before proceeding with the precipitation.

The precipitation was carried out in large test tubes. After allowing the treated sample to stand for 48 hours or after centrifuging, 51.5 ml. (equivalent to 50 ml. of the sample) of the clear, supernatant, sulphate-free sample was decanted into another test tube. Standards having the same fluoride content as those used in the Sanchis method were then made using, of course, only 50 ml. of solution. To each standard was added 1 ml. of saturated barium chloride. Each standard was then treated with 4 ml. of 6N HCl and 2 ml. of the indicator, while to each sample was added $3\frac{1}{2}$ ml. of 6N HCl and 2 ml. of the indicator. The reaction was complete in the highly acidic solution after an hour. Comparisons were made in 50 ml. Nessler tubes.

The Boruff and Abbott procedure was quite different to the above procedures. In the case of tap water, several hundred ml. were first evaporated to 50 ml. before distillation. The sample was then put in a 125 ml.

distilling flask with 20 ml. of concentrated H_2SO_4 and several glass beads. During the actual distillation the temperature was maintained at 135°C by adding small amounts of water through a dropping funnel and capillary tube attachment above the flask. When about 100 to 150 ml. of distillate were obtained, the solution was made alkaline and evaporated to 20 ml. The cold solution was then made acidic, and 20 ml. of 95 per cent alcohol were added. Several drops of 0.05 per cent alazirin indicator were added, and 0.02N HCl was added drop by drop until the color barely disappeared.

The sample was then titrated with 0.01N thorium nitrate until a faint, permanent reappearance of the color. Although this method was very accurate, more time was required for a determination since only one sample could be tested at any one time. Since about thirteen hundred fluoride determinations had to be made over a period of 60 purification runs, the two colorimetric methods were used to save time and to have a check on each sample.

Table I shows how the fluoride content of a sample of tap water varied using different procedures.

The results of Table I indicate that dilution tends to give a higher reading than that obtained with an undiluted sample. The Sandoz method is accurate to 0.2 part per million. Thus if a small mistake were made in reading the diluted sample, the error would be quite

TABLE I.

FLUORIDE CONTENT OF TAI WATER BY DIFFERENT PROCEDURES

Method	Volume of Sample ml.	Volume of Dist. H ₂ O ml.	Fluorides p.p.m.F
Sanchis	100	0	4.6
	50	50	4.8
	20	80	5.0
	10	90	5.0
	5	95	6.0
State Dept. of Health	27.5	27.5	4.8
	11	44	5.0
Boruff and Abbott	100	0	4.7
	300	0	4.6

large after multiplying by the proper dilution factor. An average of the Sanchis and State methods is probably close to the correct fluoride content.

Most of the fluoride determinations during this investigation were on the effluent waters of the purifier, with the content varying from 0 to 1.5 parts per million. Both the Sanchis and State methods were used in order to find as accurately as possible the point at which the safe limit of fluoride concentration was passed. The State method was slightly higher than the Sanchis method in most of the determinations made. When the sample was concentrated in using the State method, the results were about the same or slightly lower than the Sanchis results. Table II gives a comparison of the two methods. The samples were from various runs made during the experiment.

B. Pilot Plant Purifier

Rated Capacity. The pilot plant was rated by the International Filter Company at 275 grains of fluoride removal per cubic foot of fluorex. The high sulfate content of the water purified (150 parts per million) was taken into consideration in rating the fluorex. The pilot plant was originally supplied with 1.3 cubic feet of the material; therefore the total fluoride removal up to one part per million should be 358 grains.

In their investigations, Behrman and Gustafson found that the adsorbant continues to reduce the fluoride

TABLE II

COMPARISON OF TWO METHODS ON FLUORIDE CONTENT OF
EFFLUENT WATERS FROM THE PILOT PLANT PURIFIER

Sample No.	Sanchis 100 ml. Samp.	Fluorides p.p.m. F ⁻ S. D. H. 55 ml. Samp.	S. D. H. 225 ml. conc. to 55 ml.
96	0.3	--	0.1
102	0.3	--	0.2
39	0.2	0.5	0.4
161	0.3	0.4	0.25
169	0.4	0.5	0.3
90	0.5	0.6	--
78	0.7	0.6	--
82	0.9	1.1	--
150	1.4	1.5	--

content to 0.1 part per million or less for most of the run with the content rising to 0.6 parts per million near the end of the run. Sodium Fluoride was added to Chicago water to make the fluoride content 10 parts per million. Table III gives the data on one of their purification runs. The average fluoride content of the effluent up to 1 part per million seemed to be about 0.15 parts per million.

Actual Capacity. The actual capacity of the unit was determined by making a series of purification runs at a flow rate of 1.5 gallons per minute. As each sample was taken during the run, the time was recorded and the meter was read. From these readings, the average flow could be calculated, and any necessary adjustments could be made to keep the proper flow rate. Slight variations in the water pressure were apparent at different periods of the day. The fluorex also seemed to pack to some extent toward the end of a run. The flow rate had to be readjusted to allow for any such deviation. Table IV gives the data for a typical purification run. Graph 1 shows the relation between the effluent and the fluoride content of the effluent taken from the data of Table IV. Each run required about 17 hours.

The average fluoride content of the effluent was calculated by finding the area under the curve and dividing by the length. The average was usually around 0.42 parts per million. The capacity in grains of

TABLE III.

PURIFICATION RUN USING FLUCREX

Fluoride Content of Influent Water - 10.0 p.p.m.p.

Gallons Purified per Cubic Foot	Fluoride p.p.m. F ⁻
36	0.0
72	0.0
144	0.1
288	0.1
432	0.1
575	0.6

TABLE IV.

FLUORIDE REMOVAL USING A CONTACT FILTER OF FLUORIX

Effluent in Gallons	Rate of Flow in Gallons Per Min.	Fluoride in p.p.m.	
		Sanchis	S.D.H.
0	--	4.7	4.8
16	2.0	0.0	0.0
114	1.3	0.3	0.2
192	1.8	0.3	0.3
306	1.4	0.3	0.25
405	1.7	0.3	0.3
561	1.5	0.5	0.3
644	1.5	0.4	0.3
750	1.5	0.5	0.3
816	1.5	0.5	0.3
865	1.5	0.7	0.4
932	1.6	0.7	0.4
1,035	1.5	0.6	0.4
1,083	1.5	0.7	0.6
1,122	1.5	0.7	0.6
1,170	1.5	0.7	0.7
1,217	1.5	0.8	1.0
1,282	1.6	0.8	1.0
1,376	1.6	0.9	1.1
1,466	1.5	1.3	1.3

fluoride actually removed from the water was calculated as follows:

$$(4.8 - 0.42) (1,340) (0.058) = 341 \text{ grains}$$

The parts per million of fluorides was multiplied by 0.058 to convert to grains per gallon.

Table V shows the results obtained from other purifying runs made at about 1.5 gallons per minute flow rate. In order to find where the fluoride content of the effluent passed one part per million, curves were drawn with the scale magnified around that point. A smooth curve was drawn through the points to show where the danger point was passed. The calculations were then made on the removal capacity as was done above.

The greatest variation from the results shown in Table V is 15 grains. Since the methods of analysis were not too accurate, the above variation can not be considered too extreme. A sufficient number of runs were made to obtain an average which is probably very nearly correct. The actual capacity was 12 grains below the rated capacity. This difference is almost negligible, and it is probably due to a slight loss of material before the unit was received for this test, or to variations in the behavior of the adsorbant toward synthetic and natural waters.

These tests also indicated that the fluoride removal was not as complete as was the case in synthetic water. The average fluoride content was 0.42 whereas

TABLE V.

CAPACITY OF FLUORIDE REMOVAL AT 1.5 GALLONS PER MINUTE
FLOW RATE

Number of Purification Run	Grains of Fluoride Removal
3	341
6	344
12	356
16	345
29	342
33	351
45	343
50	341
53	348
55	352
Average	346

in the case of the synthetic water the average fluoride content of the effluent was 0.15. Such a difference could hardly be called a disadvantage since that amount of fluoride is not harmful and more water can be purified per cubic foot of material.

Effect of Flow Rate on the Capacity. The International Filter Company sets the optimum flow rate at one gallon per minute per square foot per ten inch depth of fluorex. The cross section area of the filter tank was 0.786 square feet. The depth of the fluorex was 20 inches. Therefore, the optimum flow rate for the pilot plant should be:

$$\frac{X=0.786}{1} \text{ and } \frac{Y=X}{20} \text{ or } Y=\frac{20(0.786)}{10} = 1.57 \text{ gal.per.min.}$$

where X equals gallons per minute at a depth of 10 inches of fluorex, and Y equals gallons per minute at a depth of 20 inches of fluorex. However, the company recommended a flow rate of 1.5 gallons per minute in the operation of the pilot plant.

The results obtained by operating the unit at various flow rates are shown in Table VI and on Graph II. The capacity was determined by averaging the different runs made at the same flow rate. The optimum flow rate is about 1.6 gallons per minute. A slower flow rate does not result in any appreciable gain in capacity for fluoride removal. The conclusion reached from this test would be that the flow rate recommended by the company was the optimum flow rate.

TABLE VI.

FLUORIDE REMOVAL CAPACITY OF THE PILOT PLANT AT VARIOUS
RATES OF FLOW.

Flow Rate in Gallons Per Minute	Fluoride Removal in Grains
1.20	352
1.35	354
1.40	355
1.45	348
1.50	346
1.60	347
1.68	335
1.85	328
2.00	323
2.55	290

Effect of Alkali Used Per Regeneration on Capacity.

In order to find the minimum amount of alkali that could be used per regeneration, different amounts of sodium hydroxide were used on a number of purifying runs. Just enough water was added in the caustic tank to make a 7 per cent solution. Consequently, the alkali wash was still a one per cent solution during the regeneration. Table VII and Graph II show the relation between the grains of fluoride removal and the pounds of alkali used. The experimental results indicate that the use of 1.4 pounds of alkali per regeneration is quite enough to obtain maximum capacity, yet it is not an excessive amount.

Fluoride Content of the Regeneration Wash Waters.

Fluoride determinations were made on the regeneration wash waters in order to see whether all of the fluorides were removed during regeneration, and to find the fluoride concentrations at different periods of the wash. The first part of this experiment was conducted by receiving the wash waters in calibrated carboys. The time required for each wash was recorded so that the rate of flow could be calculated. Since the amount of fluoride adsorbed from the previous purification run could be calculated, a check was possible on the amount of fluorides removed by the wash waters. Table VIII gives the data for the determination. The results from this experiment indicate that about 13 grains more of fluorides were removed

TABLE VII.

THE RELATION BETWEEN THE AMOUNT OF ALKALI USED DURING
REGENERATION AND THE CAPACITY OF FLUORIDE REMOVAL

NaOH Used in Pounds	Capacity of Fluoride Removal in Grains
0.8	312
1.0	334
1.1	328
1.3	337
1.4	340
1.6	347

from the fluorex than were added. However, this difference of about 4 per cent is within the limit of experimental error. The regeneration procedure recommended by the company was satisfactory.

Table IX and Graph III show how the fluoride concentration varies during the different regeneration steps. The function of the long downward rinse following the sodium hydroxide wash becomes apparent, since most of the fluorides were removed during this operation.

Loss of Fluorex. Fluorex is a specially prepared, reactive mixture of $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$ and hydroxy apatite ($3 \text{ Ca}_3\text{P}_2\text{O}_8 \cdot \text{Ca}(\text{OH})_2$). The material is almost completely insoluble in water, and has a density of about 30 pounds per cubic foot for the 20-40 mesh size. The high removal capacity of the fluorex is probably due to the formation of a fluorapatite by the replacement of the hydroxide radical. Regeneration would replace the hydroxide radical.

The actual loss of the fluorex was determined over a period of 50 regenerations. The material was thoroughly dried and then measured and weighed. The first weight was 70.3 pounds while the last weight proved to be 69.3 pounds. Thus, about one pound of material was lost during 50 operations. The volume at first was 1.4 cubic feet which was more than the original volume. Evidently, the material was not packed quite as much as it was originally. The volume recorded after the final run

TABLE VIII.

FLUORIDE ADSORBED BY AND REMOVED FROM FLUOREX DURING
PURIFICATION AND REGENERATION

F ⁻ Content of Influent Water 4.6p.p.m.					
Cycle Operation	Rate of Flow	Volume of Water in Gallons	F ⁻ in p.p.m.	F ⁻ added to Fluorex	F ⁻ Re- moved from Fluorex
Purifica- tion	2.0	1,334	0.43	323	-
Backwash	4.2	12.3	2.0	1.4	-
NaOH Wash	1.1	12.7	1.5	2.3	-
		2.3	4.0	0.1	-
Downward Rinse	1.0	5.0	75.0	-	20.6
		12.2	210.0	-	145.0
		5.0	320.0	-	94.2
		5.1	90.0	-	25.0
Neutrali- zation Wash	2.5	12.7	45.0	-	30.0
		12.2	30.0	-	25.0
		5.0	10.0	-	1.6
		5.2	4.0	0.2	-
		5.2	0.8	1.1	-
Total.....				328.1	341.4

TABLE IX

FLUORIDE CONTENT OF REGENERATION WASH WATERS DURING
DIFFERENT OPERATIONS

Operation	Effluent in Gallons	Rate in g. p. m.	F- in p.p.m.
Backwash	0	-	4.5
	3	5.0	4.2
	12	5.0	2.5
	21	6.	2.6
	31	6.3	2.5
NaOH Wash	1	0.9	2.4
	3	0.9	2.2
	8	0.9	3.0
	11	0.9	6.
Downward Rinse	1	0.9	1.
	4	0.9	90
	7	0.9	350
	12	0.9	510
	17	0.9	450
	23	0.9	90
	26	0.9	70
	30	0.9	70
Neutralization Wash	1	2.5	60
	11	2.7	35
	21	2.5	30
	31	2.5	1.
	40	2.5	0.5
	50	2.5	0.5

was 1.26 cubic feet. The material was packed slightly before measuring. The density of the material based on the latter figures would be 55 pounds per cubic foot.

The loss of the material was due to several causes. Although the material is only slightly soluble in water, some of the loss may be accounted for from the following calculations. Phosphates were run on the effluent waters as well as the regeneration wash waters. The average phosphate content of the influent water was 0.7 parts per million. The effluent waters had from 0.8 to 0.9 parts per million of phosphates. Thus, the gain seemed to be about 0.15 parts per million. The wash waters had a phosphate content of from 1 to 2 parts per million. The average was 1.4, or a gain of 0.7 parts per million. During the 50 cycles about 78,000 gallons of water were purified, and about 5,700 gallons were used during the regenerations. By converting the phosphate to terms of tricalcium phosphate, and then calculating the pounds gained by the water, an approximation of the loss of the material through solubility can be obtained.

$$\frac{x}{.15} = \frac{310}{62} = \frac{\text{Ca}_3(\text{PO}_4)_2}{\text{PO}_4}$$

$$\text{Purification loss} = \frac{0.15 \times 310}{62} \times \frac{0.003 \times 78,000}{7,000} = 0.48 \text{ lbs.}$$

$$\text{Regeneration loss} = \frac{0.7 \times 310}{62} \times \frac{0.05 \times 5,700}{7,000} = 0.17 \text{ lbs.}$$

$$\text{Total loss} = 0.48 + 0.17 = 0.65 \text{ lbs. of } \text{Ca}_3(\text{PO}_4)_2$$

Although this figure might be high, these calculations do indicate that there is some loss over a period of a number of purification runs.

Other losses probably took place when the material was weighed. The loss of 1.4 per cent of the material over a period of 50 cycles is not excessive. The actual losses in a large plant probably would not amount to this much, since the material would not be handled for weighing.

Drying the fluorex seemed to increase its exchange capacity to some extent. The material was not regenerated before drying, and previous to the drying process about 3,000 gallons of water were run through the material to saturate it with fluorine. After drying, the material lowered the fluoride content to 0.8 parts per million whereas, before drying, the lowering was only from 4.6 to 4.2. Evidently the fluorex undergoes some surface rearrangement during the process of drying.

Cost of Operation of the Unit. The main cost of operating a fluorex purifier would be the alkali used. The amount necessary would be 1.07 pounds per cubic foot of fluorex per regeneration. The amount of carbon dioxide used was rather hard to read, but over a period of 56 regenerations about 30 cubic feet (at 70°F) were used, or about 0.41 cubic feet per regeneration per cubic foot of material. A fluorex replacement of around 5 per cent would probably be necessary every 200-300 cycles.

If a town the size of Lubbock were to install such

a unit, the amount of fluorex required (for a water capacity of 7,000,000 gallons of water per day) would be about 6,200 cubic feet. The amount of NaOH used per day would be about 6,600 pounds, and the CO_2 would be about 2,500 cubic feet per day. Stewart found that the correct amount of lime and soda added to the water to soften it reduced the fluorides to 2.9 parts per million. Therefore, if the lime-soda softening method were used on the water before fluoride removal, only about 3,700 cubic feet of fluorex would be required, or 40 per cent less than would be required on the untreated water.

Softening and fluoride removal of Lubbock water will be impractical until all of the water can be brought to one treating plant. At the present 15 wells are scattered over the city. These wells are brought to 4 pumping stations which supply water to different parts of the city.

C. Home Purifier

Rated Capacity. According to the manufacturer of the home unit, 400 gallons of water having a fluoride content of 4 parts per million may be purified with a doubled capacity for water having 2 parts per million. The capacity for the water in question should be 800 gallons purified. Since this rating does not take into consideration the sulfate in the water, the actual capacity would be expected to be lower.

Actual Capacity. The actual capacity proved to

be only 265 gallons or 66 grains of fluoride removal. This figure is only 76 per cent of the rated capacity. After regeneration, the capacity was 47 per cent of the initial capacity. Naturally, regeneration would not be practical for a home unit. Regeneration was carried out to compare the initial capacity with the capacity after regeneration, and to test other methods of operation. The initial capacity of defluorite was found to be 55 per cent the initial capacity of the fluorex.

Although this type of filter will remove the fluorides from drinking water, there are some disadvantages to its use. No field test has been devised that will show quickly when the fluoride has exceeded one part per million. Then too, an accurate measure of the water being purified is difficult to make. The flow rate should be limited somewhat, since the recommended flow rate seems to be too fast for complete removal.

• Fluosilicate Determination

Several attempts were made during this test to find an indication of the presence of the fluosilicate in the water. The assumption was that if the ion were in the water, it would not be altered during the exchange process with the apatite. If this were the case, the ion could be recovered during the regeneration process in a concentration high enough to be determined.

The home purifier was first put through a purification run. The unit was then regenerated with 10 liters

of 0.25N KOH. The solution was made from pure KOH and distilled water. The flow rate during the wash was about 0.5 gallons per minute. A sample was taken of the influent and effluent wash waters. Silica determinations were made on the two samples as well as the fluoride content. The influent had 1 part per million of silica and no fluorides, while the effluent had 11 parts per million of silica and 152 parts per million of fluorides. Thus the silica could be converted to silicon and then to terms of fluosilicate.

$$\text{SiO}_2 = (11-1) = 10 \text{ p.p.m.}$$

$$\frac{\text{Si} = \text{Si}}{\text{SiO}_2} = \frac{28}{60} \quad 10 = 4.7 \text{ p.p.m.}$$

$$\begin{aligned} \text{Total silicon in KOH wash in grains} \\ &= (\text{liters}) (\text{gallons per liter}) (\text{grains per gallon}) \\ &= 15 \times 0.264 \times 4.7 \times 0.058 = 1.8 \end{aligned}$$

$$\begin{aligned} \text{Total fluoride in KOH wash in grains} \\ &= 15 \times 0.264 \times 152 \times 0.058 = 34.8 \end{aligned}$$

Assuming all silicon combined as fluosilicate

$$\text{SiF}_6 = \frac{1.8}{28} = \frac{X}{114}$$

(Si) (F₆)

$$X = 7.3 \text{ grains of F combined with 1.8 grains of Si}$$

Therefore, the F content of the tap water combined as SiF_6 would be $\frac{7.3}{34.8} \times 152 = 1$ part per million

The above calculations are no more than an indication that the fluosilicate ion is present in the water, but there does seem to be a possibility that the ion exists.

The titration method was attempted on the wash solution used in the above experiment. Since no inter-

fering ions were present, the writer thought that the method might work. Although positive indications were obtained that the ion was present, no accurate determinations were possible.

CHAPTER VI

CONCLUSIONS

A method of fluoride removal that might be applied to public water supplies has been tested on a small scale. The equipment was found to be simple to operate and the manufacturer's claims were checked in almost every case. Enough complete operations were made to find that the active material did not lose its removal capacity, did not change in density, and did not change appreciably in weight. The cost of operation would be mainly the cost of the alkali used. Fluoride removal used in connection with lime-soda softening would be about 60 per cent the cost that its use alone would involve.

The home purifier did not have the capacity for fluoride removal that was claimed by the manufacturer; however, the unit did seem to have a fairly high initial capacity for fluoride removal. The use of the unit would prove unreliable until a simple field test was available to show when the danger point was passed. The operation of the unit should be modified since the gravity flow rate seems to be too fast for optimum fluoride removal.

An investigation was begun on the determination of fluosilicic acid in the natural water supply. An indication was found that the ion was present in the water.

However, further work needs to be done to develop an accurate method for the determination of the fluosilicate ion.

BIBLIOGRAPHY

1. Eager, J. M.: Denti di Chiaie, U. S. Public Health Reports 16, 2576 (1901).
2. Black, G. V. and McKay, F. S.: Mottled Teeth. Dental Cosmos. 58, 132-156 (1916).
3. McKay, F. S.: Water Supplies Charged with Disfiguring the Teeth. Water Works Engineering 79, 71 (1926).
4. Smith, M. C., Lantz, E. M. and Smith, H. V.: The Cause of Mottled Enamel, A Defect of Human Teeth. Univ. of Ariz. Expt. Bull. 32, (1931).
5. Churchill, H. V.: Occurrence of Fluorides in Some Waters of the United States, Ind. Eng. Chem. 23, 996-8 (1931).
6. Dean, H. Trendly: A summary of Mottled Enamel in Texas, Texas Dental Journal, 55, 86-93 (1936).
7. Dean, H. T.: Enemic Fluorosis and Its Relation to Dental Caries. Pub. Health Rep., 66, 1443 (1938).
8. Armstrong, W. D., and Breklus, F. J.: Possible Relationship Between Fluorine Content of Enamel and Resistance to Dental Caries. J. D. Res., 17, 388-399 (1938).
9. Dean, H. T., Jay, Arnold, McClure and Elvove: Domestic Water and Dental Caries, U. S. Public Health Reports, 54, 862-88 (1938).
10. Cox, G. J., Fluorine and Its Relationship to Dental Caries, J. D. Res., 15, 401 (1938).
11. Deatherage, C. F., Klassen, C. W. and Weart, J. G.: Fluorides and Mottled Teeth in Illinois. Illinois D. J., 5, 194-200 (1938).
12. Cox, G. J.: The Fluorine and Dental Caries Problem., J. A. D. A. 27, 1107-1114 (1940).

13. Boruff, C. S.: Removal of Fluorides from Water. Ind. and Eng. Chem. 26, 69 (1934).
14. McKey, R. H. and Johnson, W. S.: Removal of Fluorides from Drinking Water. Ind. and Engr. Chem. 26, 69 (1934).
15. Fink, G. J. and Lindsay, F. K.: Activated Alumina for Removing Fluorides from Drinking Water. Ind. and Engr. Chem. 28, 947 (1936).
16. Swope, H. G. and Hess, R. H.: Removal of Fluorides from Natural Waters by Cerfluo-rite. Ind. and Engr. Chem. 29, 424 (1937).
17. Stewart, T. H.: Master's Thesis. The Removal of Fluorides from West Texas Water, 1937.
18. Adler, H., Klein, G., Lindsay, F. K.: Removal of Fluorine from Potable Water by Tricalcium Phosphate. Ind. and Engr. Chem. 30, 163-165 (1938).
19. Smith, H. V., and Smith, M. C.: Bone Contact Removes Fluorine. Water Works Engineering. Nov. 10, 1600-1603 (1937).
20. Behrman, A. S. and Gustafson, R.: Removal of Fluorine from Water. Ind. and Engr. Chem. 30, 1011-1013 (1938).
21. Sanchis, J. B.: Determination of Fluorides in Natural Waters. Ind. and Engr. Chem., Anal. Ed. 6, 134-135 (1934).
22. Boruff and Abbott: Determination of Fluorides in Illinois Waters, Ind. and Engr. Chem., Anal. Ed. 5, 236 (1933).
23. Willard, H. H., and Winter, C. B.: Volumetric Method for Determination of Fluorine. Ind. and Engr. Chem. Anal. Ed., 5, 7-10 (1933).
24. Armstrong: Ind. and Engr. Chem., Anal. Ed., 5, 300 (1933).
25. Faber, J. E., and Youngblood, C. E.: Ind. and Engr. Chem., Colorimetric Determination of Phosphates, Anal. Ed. 4, 107-108 (1932).
26. Schwartz, M. C.: Colorimetric Determination of Silica in Boiler Waters. Ind. and Engr. Chem., Anal. Ed. 6, 364 (1934).

27. Geffcken, W. and Hamann, H.: Über ein einfaches Titrationverfahren in Bestimmung von Fluor-und Ksilselfluorwasserstoff Ionen. Z. Anal. Chem. 114, 15-21 (1938).
28. Connell, C. H.; Master's Thesis. Investigation of the Natural Waters of North and West Texas for Fluorine Content, 1933.