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FLUORIDE REMOVAL FROM DRINKING WATER

Small Installations Using Virgin Bone Black

by

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CONTENTS

Abstract	2
Introduction	3
Influence of Fluorides on Health	3
Fluorides in Oklahoma Waters	5
Removal of Fluorides from Drinking Water	24
Reasons for this Investigation	25
Virgin Bone Black	25
Comparative Tests on Fluoride Removal	26
(1) Laboratory Tests	26
(2) Field Tests	27
Influence of pH on Fluoride Removal	27
Rate of Flow of Water through Filters	28
Regeneration of Filter Material	28
Odor and Taste Removal	30
Control of Filters	30
Fluoride Removal Installations	32
Conclusions	33
References	41

TABLES

I Fluoride Content in Oklahoma Water Supplies.	6
II Analyses of Waters Used in Tests	26
III Comparative Tests on Fluoride Removal	27
IV Results of Field Tests on Fluoride Removal	27
V Comparative Tests on Regeneration Methods	29

ILLUSTRATIONS

Plate I. Fluoride Removal Installation at an oil field camp.	
(a) Exterior	36
(b) Interior	36
Figure 1. Index Map of Oklahoma showing general distribution of known fluoride waters.	37
Figure 2 Sketch showing structural details of fluoride removal filter.	38
Figure 3 Sketch of portable field test unit for fluoride removal.	39
Figure 4 Sketch and Instructions for fluoride removal unit for family water supply.	40

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ABSTRACT

The mottling and discoloration of the teeth of children in certain areas has been traced to the action of fluorides in drinking water. Children under eight years of age are most susceptible to this action. Other pathological disturbances are attributed to fluorides. Excessive ingestion is capable of producing both acute and chronic poisoning. However, recent observations indicate that small amounts of fluoride in water may be beneficial. The possibility of detrimental effects has been recognized in the United States Public Health Service Drinking Water Standards which contain the statement that "the presence of fluorides in excess of 1.0 per million shall constitute grounds for rejection of the supply."

Numerous methods have been advocated for the removal of fluorides. A summary of these methods is given, including some that are in use in municipal water supply systems. No one of the methods seems satisfactorily applicable to small water supplies, especially individual homes.

The present investigation has shown that waters containing fluorides in amounts above the safe limit can be made safe through the use of virgin bone black, and at relatively low cost even for small systems. Descriptions and diagrams of simple, efficient equipment suitable for small communities, rural schools, camps, and larger homes are given; also one adapted to the smallest farm home.

A map shows the general distribution of known fluoride waters in Oklahoma. A table lists the water supplies in Oklahoma that have been found to contain as much as 0.6 part per million fluorides.

INTRODUCTION

This article has been prepared by A. L. Burwell, Chemical Engineer on the staff of the Oklahoma Geological Survey, and is based mainly upon results of an investigation undertaken by L. C. Case, Chief Chemist, and C. H. Goodnight, formerly Chemical Engineer, of the Gypsy Division, Gulf Oil Co. at Tulsa, Oklahoma.

Much of the technical detail resulting from this investigation has been intentionally omitted. Only those facts and figures have been included that have direct bearing on possible individual and community utilization of a simple process for the removal of fluorides from drinking water.

The authors express their appreciation to Mr. Robert H. Dott, Director of the Oklahoma Geological Survey, for his consideration, encouragement, and assistance in the preparation of this report; to Mr. Neal T. Dilday for the drawings and maps; to Mr. Malcolm C. Oakes for the photographs; and to Mr. H. J. Darcey, Director of the Bureau of Sanitary Engineering, Oklahoma State Health Department, for his helpful suggestions.

INFLUENCE OF FLUORIDES ON HEALTH

The mottling and discoloration of teeth of children living in certain localities is the result of fluorides contained in the drinking water. This correlation was established by H. V. Smith and co-workers at the University of Arizona, and the findings were published in 1931¹. Fluoride absorption by the human body is related to the aqueous solubility of the fluoride salt and its state at time of absorption. Pathological changes attributed to fluoride absorption are in the nature of osteosis, generally, but excessive ingestion of fluorides is capable of producing both acute and chronic poisoning. 180 parts per million has a toxic effect, 2 to 3 parts per million causes retention of the fluorides, 1.2 parts per million causes mottled enamel, while 0.6 part per million is without effect.² Therefore, the acceptable limit for fluorides in drinking water has been set at 1.0 part per million.³ This limit is well above the fluoride content recommended by some investigators as beneficial in the control of tooth decay. This recommendation has been receiving considerable attention but its advocates acknowledge that "the fluoride-dental caries hypothesis upon which it is based still has not been proven." 4,5

A study of the distribution of endemic fluorosis in Oklahoma was made by H. Tendley Dean, Dental Surgeon of the U. S. Public Health Service, assisted by E. C. Warkentin, Assistant Sanitary Engineer, Oklahoma State Health Department. The results are given in Chemical Analyses of Oklahoma Waters published in 1942 as Oklahoma A & M College Engineering Experiment Station Publication No. 52. Quotations following are from this report, which, together with the accompanying map, will indicate where the waters of relatively high fluoride content are found, and communities where school authorities may well give consideration to the installations of small fluoride-removal units described in the present report.

"When small quantities of fluorides are taken into the body in the water or in the food, the fluoride is deposited in the teeth and the bones. It makes its presence visible in the discoloration of the teeth. This may vary from mild, chalky, or dark appearing stains to deep pits, very darkly colored, with destruction of the enameled surfaces. Children reared in those areas where the water contains fluoride of greater concentration than one part per million are likely to have disfigurement.

"Children who continuously drink water containing above one part per million of fluoride throughout the period of formation of the permanent teeth, i.e., between the ages of three months and eight years, probably will have teeth badly stained and disfigured. When badly affected, the enamel of the teeth is softened and destroyed in spots.

"Evidence is fairly clear and convincing that the enamel of children's teeth is altered and that the bones of the body may be affected when fluorides are ingested over a long period of years. Evidence of just how small an amount of fluoride, or how long a time of ingestion is required before there is an apparent discoloration of the teeth, is not yet definitely determined. As in all diseases, individuals vary in susceptibility; some show effects very quickly, while others are immune.

"No water containing more than one part per million of fluoride can be used continuously by children below the age of eight years without the risk of permanently disfiguring and harming the teeth. Adults apparently are not affected by this, or a much greater concentration. This value of one part per million repre-

period of years; high quantities of fluorides may be ingested in water or food for short periods of time without affecting the enamel materially, provided there are correspondingly long periods when water of low fluoride content is used.

"Thus, any supply that has as much as one part per million of fluorides should not be considered safe water for children to use. Another source of water should be obtained or steps taken to remove the fluoride from the water for children in the school and in the home.

"Those interested in having water tested for fluoride may communicate with the Sanitary Engineering Bureau, Oklahoma State Health Department, Oklahoma City, Oklahoma for information and direction in the collection of the sample.

"Practically all the municipal water supplies of the state have been tested for fluorides and the amounts observed are shown in the table at the end of this chapter.

"There are several areas in Oklahoma where mottled enamel is prevalent, namely:

- (1) In the Panhandle counties, which section is apparently an extension of the well known region of occurrence in the Panhandle of Texas.
- (2) In a restricted rural group residing along the east bank of the North Fork of the Red River.
- (3) The north side of the Red River in Tillman County. This is associated with water from dug, shallow wells.
- (4) Sections of Comanche County. These wells contain the highest concentration of fluoride reported in the state.
- (5) An area in the extreme northeastern section of the state, extending from Vinita and Bluejacket northward. Here mottled enamel is associated with the use of domestic wells, 1200 to 1500 feet deep."

A 6th. area, analyses having been made since the publication of the above, lies in western Carter County.

FLUORIDES IN OKLAHOMA WATERS

The following list (Table 1), compiled from Table VIII of the fore-mentioned Chemical Analyses of the Waters of Oklahoma and later analyses by the State Health Department and the Ground Water Division of the U.S. Geological Survey, shows water supplies by towns, which contain more than 0.6 part per million fluoride. The same data are generalized on the accompanying map. (Fig-

TABLE 1
Fluoride Content in Oklahoma
Water Supplies, with 0.6 part per million or More

Town or County	Date of Analysis	Source of Water	Depth of Well	Fluorides p.p.m.
Afton (Ottawa County)	6-7-38	Well	1200'	1.4
Alfalpa County	5-5-38	Salt Fork of the Arkansas River, 500 feet upstream from Great Salt Plains Dam Axis		0.8#
	7-22-38	Do.		0.9#
	7-22-38	Well point, approximately 1/4 mile north of river		0.6#
Allen (Pontotoc County)	8-18-32	Well	427'	2.2#
	2-21-42	Well (Municipal supply), tap at pump station	500'	2.2#
	1-4-43	Municipal water supply tap at pump station		2.6#
Alva (Woods County)	3-21-40	Well (Starr No. 1)		0.8#
	3-21-40	Well (Starr No. 2)		0.8#
	3-21-40	A. B. Campbell		0.7#
Apache (Caddo County)	10-7-36	Municipal Water Supply, (Public Works Project No. 3673)		1.4#
Atoka (Atoka County)	11-1-34	Muddy Boggy Creek		0.8
Beaver County	11-28-39	Well (Oklahoma Nat. Gas Pipe Line Co. Sec. 15, T. 1 N., R. 20 ECM)	380'	1.3*
	11-28-39	Well (J. W. Mounts. Sec. 21, T. 1 N., R. 21 ECM)	245'	1.4*

11-28-39	Well (Blue Mound School Dist., Sec. 21, T. 1 N., R. 22 ECM)	180'	1.0*
11-29-39	Well (W. A. Getz, Sec. 15, T. 1 N., R. 24 ECM)	197'	1.1*
11-28-39	Well (F. J. Howard, Sec. 24, T. 2 N., R. 20 ECM)		0.7*
11-28-39	Well (J. W. Ollenberger, Sec. 21, T. 2 N., R. 21 ECM)	164'	0.6*
11-28-39	Well (Bolko School Dist. 75, Sec. 16, T. 2 N., R. 22 ECM)	175'	1.4*
4-5-40	Well (J. F. Hosler, Sec. 21, T. 2 N., R. 26 ECM)	150'	0.6*
4-5-40	Well (Roy Anderson, Sec. 27, T. 2 N., R. 27 ECM)	66'	0.9*
11-28-30	Well (W. J. Phelps, Sec. 14, T. 3 N., R. 22 ECM)	50'	0.6*
4-5-40	Well (E. E. Wells, Sec. 25, T. 3 N., R. 27 ECM)	23'	0.8*
4-8-40	Well (L. H. Donley, Sec. 22, T. 4 N., R. 20 ECM)	153'	1.2*
11-29-39	Well (Bertha McCool, Sec. 29, T. 4 N., R. 25 ECM)	48'	0.9*
4-8-40	Well (J. A. Hershey, Sec. 27, T. 5 N., R. 20 ECM)	150'	2.9*
4-8-40	Well (Mrs. B. L. Lewis, Sec. 14, T. 5 N., R. 22 ECM)	103'	0.8*
4-4-40	Well (Sec. 15, T. 5 N., R. 28 ECM)	36'	0.8*
4-8-40	Well (H. H. Matkin, Sec. 20, T. 6 N., R. 20 ECM)	159'	2.9*
4-8-40	Well (A. T. Dirks, Sec. 29, T. 6 N., R. 20 ECM)	189'	0.7*

	4-9-40	Well (J. Childers, Sec. 34, T. 6 N., R. 23 ECM)	114'	1.0*	∞
	4-3-40	Well (XIT Ranch, Sec. 33, T. 6 N., R. 25 ECM)	40'	0.8*	
	4-4-40	Well (Otto Barkley, Sec. 30, T. 6 N., R. 27 ECM)	65'	0.7*	
Bethany (Oklahoma County)	4-16-43	Baker Industries	608'	0.8*	
	7-23-32	Well	50'	0.7	
Blaine County	3-18-42	Well (Sec. 4, T. 14 N., R. 11 W.)	25'	0.6*	
	3-18-42	Well (T.M. White, Sec. 11, T. 14 N., R. 11 W.)	37'	0.6*	
	3-18-42	Well (A. B. Hume, Sec. 20, T. 14 N., R. 11 W.)	35.1'	1.0*	
	3-18-42	Well (Lloyd Smith, Sec. 36, T. 14 N., R. 11 W.)	25'	1.3*	
	3-18-42	Well (R. E. Vowell, Sec. 34, T. 15 N., R. 11 W.)	17'	0.7*	
	3-18-42	Well (F. F. Sheppard, Sec. 35, T. 15 N., R. 11 W.)	27'	2.0*	
Bluejacket (Craig County)	4-25-39			3.6	
Boise City (Cimarron County)	12-22-37	Well (Air Lift, Cimarron Utilities Company)		1.2#	
	10-14-38	Well	165'-382'	1.3	
	12-22-37	Well No. 1 (Cimarron Utilities Co.)		1.3#	
	9- -38	Well	165'-382'	1.2	
	4-16-38	Well		1.3	
	1-5-38	Well		0.8	
	12-31-37	Well No. 1	171'	1.3	
	12-31-37	Well (Air lift)	382'	1.2	
	10-24-32	Well	165'-382'	1.8	

	10-24-32	Well (A.T.-S.F.R.R.)		2.0
	11-9-38	Well (Public Supply, Cimarron Utilities Co.)	167'	1.0
Brinkman (Greer County)	4-25-32	Well	15'	0.9
Bristow (Creek County)	8-18-32	Well	100'-220'	0.8
Britton (Oklahoma County)	4-16-43	City well	803'	2.6*
Buffalo (Harper County)	12-3-34	Springs		1.0
Byars (McClain County)	5-25-40	Well No. 1		0.6
Canadian County	3-7-42	Well (Fred Smith, Sec. 3, T. 12 N., R. 5 W.)	31'	0.9*
	3-17-42	Well (Sec. 8, T. 12 N., R. 5 W.)	27'	2.8*
	3-7-42	Well (Douglas Davis, Sec. 14, T. 12 N., R. 5 W.)	34'	1.1*
	3-17-42	Well (W. C. Larkin, Sec. 23, T. 12 N., R. 5 W.)		0.6*
	4-17-42	Well (Harry Cooksey, Sec. 2, T. 12 N., R. 7 W.)	46'	0.9*
	3-17-42	Rich Valley School (Sec. 12, T. 12 N., R. 7 W.)	32'	0.9*
	4-15-43	Well (U.S.G.S. Obs., Sec. 21, T. 12 N., R. 7 W.)	20.4'	0.8*
	4-16-43	Well (Claude Branch, Sec. 6, T. 13 N., R. 8 W.)	11'	1.6*
	3-17-42	Well (George Wilkowske, Sec. 22, T. 13 N., R. 8 W.)	17'	0.6*
	4-16-43	Well (Cheyenne, Arapaho Indian Agency, Sec. 24, T. 13 N., R. 8 W.)	180'	0.7*
	4-16-43	Well (Stough, Sec. 34, T. 14 N., R. 9 W.)	32'	0.8*

Carter County

4-16-43	Well (U.S.G.S. Obs., Sec. 15, T. 14 N., R. 10 W.)	20.9'	0.7*
3-18-42	Well (Annie Dillion; Sec. 17, T. 14 N., R. 10 W.)	14'	1.6*
5-25-42	Well (William Mabry, Sec. 22, T. 14 N., R. 10 W.)	21'	2.6*
3-16-42	Well (William Mabry, Sec. 22, T. 14 N., R. 10 W.)	21'	3.4*
4-16-43	Well (Sid Morris, Sec. 25, T. 14 N., R. 10 W.)	27'	1.7*
2-1-38	Well (Will H. Smith, Sec. 31, T. 2 S., R. 3 W.)		1.3
2-1-38	Well (Magnolia Lease, Sec. 26, T. 2 S., R. 3 W.)		1.7
2-1-38	Well (Will H. Smith, Sec. 26, T. 2 S., R. 3 W.)		1.0
1-22-38	Well (Will Smith Lease, Sec. 27, T. 2 S., R. 3 W.)		1.3#
1-7-37	Well (Magnolia 1600, Sec. 19, T. 1 S., R. 3 W.)		0.7
1-4-38	Well (Magnolia 1600, Sec. 19, T. 1 S., R. 3 W.)		0.7#
1-7-37	Well (Carter Camp, Sec. 19, T. 1 S., R. 3 W.)		0.7
1-4-38	Well (Carter Camp, Sec. 19, T. 1 S., R. 3 W.)		0.7#
1-21-38	Well (Lone Star Camp, Sec. 38 T. 2 S., R. 3 W.)		3.0
1-7-38	Deep well (Texas Co. Lease)		2.0#
12-31-37	Well (Magnolia Deep Well) 500' Layman Farr		3.9

	1-22-38	Well (Magnolia Lease, Sec. 31, T. 2 S., R. 3 W.)		1.7#
	12-31-37	Well (Empire Camp, 500')		3.5
	9- -38	Well (Empire Camp, 500')		3.5
Chickasha (Grady County)	12-30-39	Sample marked "1227 So. 7th. C. E. Plott"		1.5#
Cimarron County	11-10-38	Well (James Dove, Sec. 32, T. 1 N., R. 3 ECM)	59'	1.3*
	4-14-39	Well (State of Oklahoma, Sec. 7, T. 1 N., R. 4 ECM)	122'	1.0*
	11-9-38	Well (Fred Brakhage, Sec. 20, T. 1 N., R. 5 ECM)	78'	2.0*
	11-9-38	Well (State of Oklahoma, Sec. 28, T. 1 N., R. 7 ECM)	221'	2.0*
	11-9-38	Well (W. P. Foreman, Sec. 29, T. 1 N., R. 7 ECM)	158'	2.1*
	4-15-39	Well (Ernest Tatman, Sec. 4, T. 1 N., R. 8 ECM)	300'	1.2*
	11-10-38	Well (E. R. Blake, Sec. 15, T. 1 N., R. 9 ECM, furnishes Griggs School)	300'	2.1*
	4-14-39	Well (J. C. Lujan, Sec. 25, T. 2 N., R. 1 ECM)	23'	4.3*
	4-14-39	Well (J. G. Mayhan, Sec. 33, T. 2N. R. 2 ECM)	7.5'	1.2*
	4-14-39	Well (J. E. Heatley, Sec. 18, T. 2 N., R. 3 ECM)	120'	1.4*
	4-18-39	Well (Prudential Life Ins. Co., Sec. 2, T. 2 N., R. 5 ECM)	125'	1.5*
	4-9-38	Well (W. B. Sizemore, Sec. 4, T. 2 N., R. 6 ECM)	141'	2.2*
	11-9-38	Well (C. J. Taggert, Sec. 2, T. 2 N., R. 7 ECM)	152'	3.8*

11-10-38	Well (Plainville Consol. School, Sec. 28, T. 2 N., R. 8 ECM)	263'	2.5*	15
11-10-38	Well (Sandy View Consol. School, Sec. 10, T. 3 N., R. 4 ECM)	182'	1.3*	
4-18-39	Well (Thomas Potts, Sec. 27, T. 3 N., R. 6 ECM) furnishes Garlington School	160'	1.8*	
11-10-38	Well (T. F. Phillips, Sec. 2, T. 3 N., R. 7 ECM)	320'	1.8*	
11-10-38	Well (Mrs. Wesley Burch, Sec. 3, T. 3 N., R. 7 ECM)	100'	3.6*	
4-15-39	Well (Frank Outhier, Sec. 27, T. 3 N., R. 8 ECM)	242'	4.5*	
4-15-39	Well (Roy Hanes, Sec. 13, T. 3 N., R. 9 ECM), furnishes Midway School	198'	3.1*	
11-10-38	Well (A. M. Payne, Sec. 16, T. 3 N., R. 9 ECM)	206'	2.1*	
11-13-38	Well (J. L. Donley, Sec. 12, T. 4 N., R. 3 ECM)	205'	1.9*	
11-11-38	Spring (J. A. James, Sec. 4, T. 4 N., R. 4 ECM)		1.3*	
11-13-38	Spring (Sec. 5, T. 4 N., R. 4 ECM)		1.4*	
4-14-39	Well (M. M. Adees, Sec. 23, T. 4 N., R. 4 ECM)	116'	2.7*	
11-17-38	Well (H. A. Schneider, Sec. 15, T. 4 N., R. 5 ECM)	215'	2.2*	
4-18-39	Well (Bruce Wood, Sec. 31, T. 4 N., R. 6 ECM)	149'	1.7*	

4-18-39	Well (Mrs. Lewis Bruning, Sec. 29, T. 4 N., R. 7 ECM)	103'	2.1*
11-9-38	Well (N. W. Ford, Sec. 22, T. 4 N., R. 9 ECM), Lone Star School District #31.	273'	1.1*
4-14-39	Well (H. G. Willson, Sec. 6, T. 5 N., R. 4 ECM)	18'	2.7*
4-14-39	Spring (George W. Gillis, Sec. 21, T. 5 N., R. 4 ECM)		3.6*
4-13-39	Well (B. N. North, Sec. 4, T. 5 N., R. 5 ECM)	13'	1.3*
11-17-38	Well (Mrs. J. Martin Ford, Sec. 12, T. 5 N., R. 5 ECM)	15'	1.6*
4-13-39	Spring (Flag, Sec. 32, T. 5 N., R. 5 ECM)		1.2*
4-15-39	Well (John Copper, Sec. 15, T. 5 N., R. 7 ECM, furnishes Burnett School, District #7)	143'	2.0*
4-15-39	Well (Edward Jermyn, Sec. 18, T. 5 N., R. 8 ECM, water for Berg School)	280'	2.0*
11-9-38	Well (W. H. Greaser, Sec. 8, T. 5 N., R. 9 ECM)	295'	2.4*
4-15-39	Well (G. A. DeHann, Sec. 22, T. 5 N., R. 9 ECM, furnishes Harmony School District #22 and residents of Sturgis)	239'	3.3*
4-13-39	Spring (Myrtle Tharp, Sec. 33, T. 6 N., R. 1 ECM)		1.4*
4-13-39	Spring (Cowboy College, Sec. 28, T. 6 N., R. 3 ECM)		1.6*
4-13-39	Spring (Harry Clark, Sec. 33, T. 6 N., R. 4 ECM)		1.1*

	4-13-39	Well (A. S. Parker, Sec. 23, T. 6 N., R. 5 ECM)	205'	1.5*	14
Duncan (Stephens County)	8-18-32	Well No. 5		2.2	
	8-18-32	Well No. 4		1.0	
Edmond (Oklahoma County)	4-15-43	City Well No. 5	751'	1.8*	
Elk City (Beckham County)	9-15-38	Wells		1.0	
	11-20-36	Well No. 1		1.2	
	11-20-36	Lake on Elk Creek		1.2	
	12-3-34	Lake on Elk Creek		1.2	
	3-31-33	Lake on Elk Creek		0.9	
	3-31-33	Lake on Elk Creek		0.8	
	9-15-38	Municipal Water Supply - wells and reservoir		1.0*	
El Reno (Canadian County)	11-14-38	Well No. 4	49'-54'	1.0	
	11-14-38	Well No. 5	49'-54'	1.0	
	11-14-38	Well No. 6	49'-54'	1.3	
	11-14-38	Well No. 8	49'-54'	1.0	
	11-14-38	Well No. 9	49'-54'	1.0	
	11-14-38	Well No. 10	49'-54'	0.9	
	11-14-38	Well No. 11	49'-54'	1.1	
	11-14-38	Well No. 12	49'-54'	0.9	
	9- -38	Well	49'-54'	0.8	
	5-13-38	Well No. 11		0.8	
	7-27-32	Well No. 7		1.0	
	7-27-32	Well No. 5		0.7	
	3-3-42	City Well	50'	1.0*	
	5-3-38	Well No. 11, U. S. Southwest Reformatory		0.8*	

Fairview (Major County)	11-1-34	Springs		1.0
Faxon (Comanche County)	7-20-38	Well near Faxon	238'	2.0#
Felt (Cimarron County)	11-22-37	Cimarron Utilities Company		2.6#
	11-10-38	Well (Public Supply, Cimarron Utilities)	132'	1.2*
	1-5-38	Cimarron Utilities Company		1.4#
	1-21-38	Well	125'-132'	1.4
	4-16-38	Cimarron Utilities Company		0.9#
	1-5-38	Well		1.4
	12-31-37	Well (School)		1.2
	12-31-37	Well (A.T.-S.F.R.R.)		1.4
	9- -38	Well	125'-132'	1.4
	5- -32	Well	125'-132'	1.3
Foraker (Osage County)	12-17-34	Well	860'	1.0
Forgan (Beaver County)	10-32	Well (South)	85'	0.6
Fox School in Carter County	9- -38	Well	500'	2.8
			(abandoned)	
	9- -38	Well	140'	1.0
	2-4-38	Well	140'	1.0
	12-16-37	Deep well		2.8
Frederick (Tillman County)	6- -32	Well No. 3	61'	0.8
	6- -32	Well No. 9	61'	0.7
	6- -32	Well No. 2	61'	0.7
Geary (Blaine County)	5-25-42	City well	34'	1.0*

Goodwell (Texas County)	3-4-42	City well	34'	0.8*	
	10-1-37	Well (Panhandle A & M College)		0.8#	
	9- -38	Well	188'	1.6	
	10-1-37	Municipal water supply		1.2#	
	4-16-38	Well		1.2	
	11-22-37	Well (farm, Panhandle, A & M College)		0.6#	
	12-31-37	Well	188'	1.6	
	12-31-37	Well (C.R.I. & P. Ry.)		1.7	
	6-28-37	Well	188'	1.6	
	10- -32	Well		1.5	
Guymon (Texas County)	2-2-38	City well	188'	1.8*	
	11-4-39	Well No. 1	190'	2.0	
	10-1-37	Well (Okla. Elec. & Water Co.)		1.2#	
	11-4-39	Well No. 2	190'	1.9	
	10-27-37	Well (Swimming pool near North Canadian River)	55'	1.0#	
	11-4-39	Well No. 3	125'	1.4#	
	9- -38	Well	330'-400'	1.8	
	4-16-38	Well		1.6#	
	12-31-37	Well (Okla. Elec. & Water Co.)		1.7#	
	10- -32	Well	330'-400'	1.5	
	3-2-40			3.0#	
	1-11-40	Well No. 3		1.3#	
	11-27-37	Well (Public Supply, Okla. Elec. & Water Co.)	330'	1.7*	
	Hardesty (Texas County)	11-22-37	School well		0.8#

	4-16-38	School well		1.2#
	4-16-38	Town well		1.6#
	11-27-37	Well, public supply		1.4*
Healdton (Carter County)	9- -38	Well	400'	2.6
	1-7-38	Well		2.6#
	12-3-34	Well	400'	2.6
	2-7-41	Vicinity of		5.0#
Hennessey (Kingfisher County)	6-11-39	Park Well No. 1		1.2
	10-29-36	Payne Well NO. 1		1.8#
	6-11-39	Payne Well		0.9
	11-5-36	Park Well No. 2		1.1#
	6-11-39	Turkey Creek Well		0.8
	11-5-36	Park Well No. 1		1.3#
	6-11-39	Park Well No. 2		1.3
	11-6-36	Park wells		1.3#
	9- -38	Well	41'-72'	1.2
	11-6-36	Payne Well No. 1		1.6#
	12-1-36	Well (Mixed)	41'-72'	1.2
	8-11-39	Municipal consolidated supply		0.9#
	12-1-36	Well (Payne)		1.3
	12-1-36	Well (Park)		1.0
	1-23-32	Well	41'-72'	1.2
Hollis (Harmon County)	0-9-38	Springs		0.6
	7-13-38	Wells (shallow)		0.6
Hooker (Texas County)	11-22-37	Municipal water supply		0.6#
	9- -38	Wells	220'-280'	0.6-0.3

Indiahoma (Comanche County)	10- -30	Well	216'	0.7	19
	2-18-42	Municipal well	900'	6.5	
	1-4-43	Well (H. J. Bland)	400'	10.0#	
Kenton (Cimarron County)	4-13-39	Well (Kenton School, U. G. Dist. #1, Sec. 16, T. 5 N., R.1 ECM)	80'	2.3*	
Keyes (Cimarron County)	11-22-37	Cimarron Utilities Co.		2.0#	
	9- -38	Well	220'-210'	1.6	
	11-22-37	A. Burk		1.5#	
	4-16-38	Well		1.7	
	4-16-38	Cimarron Utilities Co.		1.7#	
	1-21-38	Well	200'-210'	1.6	
	1-5-38	Well		1.6	
	11-9-38	Well (Public supply, Santa Fe R.R., Sec. 12, T. 4 N., R. 7 ECM)	139'	2.7*	
Lawton (Comanche County)	9-14-40	Well	650'	9.0	
	12-4-39	Well near Lawton, sample marked "Well L1"	1000'	10.0#	
	1-24-40	J. M. Stevens well	1609'	11.0	
	12-4-39	Bed of Medicine Creek near Lawton		0.8#	
	1-24-40	J. M. Stevens well	846'	10.0	
	4-2-40	Sample submitted by Walter W. Silcott		0.9#	
	1-24-40	M. Kochler well		11.0	
	8-30-40	Artesian well in vicinity of Lawton		10.0	
	12-12-39	Wells on Flat Iron Tract	30'	1.2	

	12-22-42	Municipal water supply		3.8#
	11-29-39	Cameron well	1600'	11.0
McLoud (Pottawatomie County)	11-29-39	Stephens well	1400'	12.0
	1-25-38	Deep well		0.9
	7-27-32	Well No. 1	39'-48'	0.7
	7-27-32	Well No. 2	39'-48'	0.7
	11-13-41	Municipal supply		1.5
	11-13-40	Municipal supply		1.2
	12-23-37	Proposed well		1.9#
	1-3-38	Proposed well	300'	0.8#
	11-13-40	Deep well		1.2#
	11-13-40	Municipal water supply, tap in cafe		1.5#
	1-4-43	Municipal water supply		1.3#
Maud (Pottawatomie County)	2-3-40	Wells		5.5#
Miami (Ottawa County)	5-6-43	Wells (Northeastern Okla. Jr. College)		0.6#
Nichols Hills (Oklahoma County)	12-21-39	Well No. 1		1.2
	12-4-39	Well No. 2		2.4#
	12-21-39	Well No. 2		1.2
	12-21-39	Well No. 3		2.2
	12-4-39	Well No. 3		0.8#
	12-21-39	Well No. 4		1.0
	4-16-43	City Well No. 3	816'	1.0*
	12-29-42	Well No. 5		4.8#

	4-16-43	City Well No. 5	815'?	2.9*	20
	12-29-42	Warehouse tap		2.2#	
West Nichols Hills (Oklahoma County)	2-28-41	Well		0.6#	
	12-29-42	Water sample from pump discharge		0.6#	
Noble (Cleveland County)	3-9-43	City well	461'	1.3*	
Norman, City (Cleveland County)	3-8-43	City well (Rich St. & Santa Fe RR)	591'	0.6*	
	3-6-43	City well (Tower Well)	567'	3.4*	
	9- -38	Well	525'-650'	0.7	
	1-31-38	Wells	350'-600'	0.7#	
	1-1-38	Well	525'-650'	0.7	
	11-3-37	Well	525'-650'	0.7	
	4-8-32	Well	525'-650'	1.0	
Norman, N.A.T.T.C. (Cleveland County)	3-11-43	Well No. 2	562'	2.4*	
	3-11-43	Well No. 3	458'	2.8*	
Norman, University of Oklahoma	3-10-43	Well No. 3	661'	2.2*	
Oklahoma City (Oklahoma County)	7-17-40	University Hospital Well		1.0	
	5-18-32	Lake Overholser		0.6	
	7-17-40	University Hospital Deep Well		1.0#	
	11-23-40	University Hospital Deep Well		1.2#	
	11-7-40	University Hospital Deep Well		1.1#	
	10-7-40	University Hospital Deep Well		1.1	
Oklahoma County	3-7-42	Well (Sec. 6, T. 11 N., R. 3 W.)	21'	0.9*	
	6-21-43	Koller Construction Co. Well No. 3		0.6#	

	3-7-42	Well (S. W. Manell, Sec. 33, T. 12 N., R. 4 W)	27'	1.4*
	4-16-43	Skelly Oil Co. Well (NE $\frac{1}{4}$, NE $\frac{1}{4}$, Sec. 31, T. 11 N., R. 2 W)	765'	0.6*
Pauls Valley (Garvin County)	3-31-38	Well No. 2		0.6
Plainview (Beaver County)	4-16-38	Well, School		1.9#
Prague (Lincoln County)	7-27-32	Well (plant)		1.0
	7-16-43	Municipal water supply		0.6#
	7-27-32	Well (grade school)		0.7
Quapaw (Ottawa County)	5-4-40	City wells		0.8
Rush Springs (Grady County)	3-25-40	Well	26'	0.7#
Stratford (Garvin County)	4-8-32	Well	300'	0.7
Texas County	11-8-37	Well (Sunny Side School, Sec. 21, T. 1 N., R. 11 ECM)		2.0*
	1-25-38	Well (Mrs. R. Ritter, Frisco School, Sec. 10, T. 1 N., R. 14 ECM)	100'	1.8*
	2-2-38	Well (Clem Huddelston, Sec. 26, T. 3 N., R. 11 ECM)	140'	3.8*
	11-10-37	Well (Liberty School Dist. 93, Sec. 5, T. 3 N., R. 12 ECM)		4.8*
	11-27-37	Well (S. Pleasant View School, Sec. 10, T. 3 N., R. 17 ECM)		1.2*
	11-1-37	Well (C. Dencker School, Sec. 9, T. 4 N., R. 10 ECM)	200'	1.9*

	12-17-37	Well (Center School Dist. 147, Sec. 17, T. 4 N., R. 11 ECM)	225'	2.2*
	1-26-38	Well (Friendship School Dist. 80, Sec. 4, T. 4 N., R. 13 ECM)	151'	1.1*
	12-17-37	Well (L. J. Guymon, Triumph School, Sec. 25, T. 5 N., R. 11 ECM)	150'	1.0*
	12-17-37	Well (C. T. Fowler Well, School, Sec. 9, T. 5 N., R. 12 ECM)	220'	2.1*
	3-22-38	Well (Blake well, school, Sec. 11, T. 5 N., R. 13 ECM)	207'	1.0*
	3-22-38	Well (Brown's Corner & Comet Schools, Henry Hiller well, Sec. 13, T. 5 N., R. 13 ECM)	240'	0.6*
	12-4-37	Well (Phoenix School, Sec. 35, T. 5 N., R. 18 ECM)		1.5*
	3-22-38	Well (C. E. Garrett well, Pleasant Plains School, Dist. 68, Sec. 22, T. 6 N., R. 13 ECM)	230'	0.7*
	12-23-37	Well (Buena Vista School, Sec. 20, T. 6 N., R. 18 E.)	134'	0.8*
Texhoma (Texas County)	11-22-37	Well (Cimarron Utilities Co.)		1.4*
	9- -38	Well	230'	1.1
	4-16-38	Well		1.1
	1-21-38	Well	230'	1.1
	1-5-38	Well		1.1*
	10-24-32	Well	230'	1.5
	1-5-38	Well (Cimarron Utilities Co.)		1.1*
	2-2-38	Well, Public Supply (Cimarron Utilities Co.)	230'	1.0*
	4-16-38	Well (Cimarron Utilities Co.)		1.1*

Tipton (Tillman County)	5-27-32	Well No. 1	90'	0.9
Turpin (Beaver County)	11-22-37	School well		1.1#
	4-16-38	School well		1.3#
Tyrone (Texas County)	9- -38	Well	250'	0.8
	11-22-37	Municipal Water Supply		0.9#
	10-24-32	East Well	300'	1.2
	10-24-32	West Well	300'	0.8
	8-6-38	Well	285'	0.8*
Wapanucka (Johnston County)	5-3-32	Well	16'	0.9
Warr Acres (Oklahoma County)	12-29-43	Well No. 3, pump discharge		0.6#
Wewoka (Seminole County)	12-19-38	Sample submitted by J. E. Ryan 10 miles from Wewoka		0.8#
	12-19-38	Sample submitted by J. L. Shepherd, 317 W. 7th. St.		1.1#
Woodward (Woodward County)	7-16-43	Municipal Water Supply		0.8#
Woodward County	5-24-38	Ft. Supply dam site, 1600', upstream from proposed dam axis		0.7#
Wynona (Osage County)	6-13-32	South well	385'	0.6
Yukon (Canadian County)	5-11-32	Well	32'-46'	0.6
	3-17-42	Well, City	43'	0.8*

*Analysis by United States Geological Survey

#Recent analysis by Oklahoma State Health Department laboratory

REMOVAL OF FLUORIDES FROM DRINKING WATER

The earliest methods for the removal of fluorides from drinking water were based upon treatment of the water with chemicals capable of precipitating insoluble fluorine compounds, followed by sedimentation and filtration. Boruff added excess alum and lime to the water, and also tried agitation of the water with activated alumina.⁶ Fink and Lindsay passed the water through a bed of activated alumina and found that the fluorides were absorbed but that the efficiency of the material was less with water of high pH value.⁷ Patents were issued on the use of activated alumina.⁸

McKee and Johnston used several different kinds of carbon in their experiments, and found that activated carbons gave the best results but were more efficient when the pH was kept low.⁹⁻¹⁰ Smith, et al, conducted a number of experiments with processed bone (Bone meal) and reported a method wherein the processed bone was boiled in dilute caustic soda, washed and neutralized, calcined, then rewashed with acid, whereby a product was obtained capable of removing fluorides from water.¹¹⁻¹² About this same time, Elvove advocated the use of either tricalcium phosphate or magnesia for the purpose.¹³ Various forms of tricalcium phosphate and apatite were tested for fluoride removal by McIntire and Hammond, and patents taken out on several of these.¹⁴⁻¹⁵

Efforts to prepare a still more satisfactory product led Adler, Klein and Lindsay to prepare a special calcium phosphate, porous and granular in form, said to be essentially a mixture of hydroapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$, and tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, and to be twice as efficient as activated alumina for fluoride removal.¹⁶

When water containing fluorides is passed through a bed of this special calcium phosphate, the fluorides are absorbed or combine chemically, and the effluent water should be practically free from fluorides if the necessary control has been exercised. Advocates of this material state that the pH of the influent water has no influence on its efficiency for fluoride removal and irrespective of the pH of the influent water, the effluent water is always approximately 7.0¹⁶

This special calcium phosphate has been used in numerous fluoride-removal installations. The high cost of the material is offset, at least partially, by a process of regeneration in which the absorbed fluorides are removed by washing with a caustic soda solution. Residual caustic is neutralized by a weak acid wash, preferably carbonic acid (carbon dioxide). The absorption capacity is thus partially regenerated and the material may then be used again. It is claimed that a considerable number of regenerations can be made without undue loss of efficiency.¹⁷⁻¹⁸⁻¹⁹

Patent rights on the use of tricalcium phosphate for the removal of fluorides from water have been granted to Elvove and assigned to the U.S. Government.²⁰

A discussion of the removal of fluorides, including some of the methods just described, is given by Warkentin in Chemical Analyses of Waters of Oklahoma. (pp. 73-74)

REASONS FOR THIS INVESTIGATION

The fact that special calcium phosphate material, when used to treat a certain water that served as a water supply for an oil-field camp, did not produce satisfactory fluoride removal and did not regenerate satisfactorily when subjected to the prescribed method, led Case and Goodnight to study the subject further. During the study they investigated the fluoride-absorption capacity and regeneration possibilities of Virgin Bone Black in comparison with the special calcium phosphate material.

VIRGIN BONE BLACK

Virgin bone black, also called animal charcoal, is a porous, amorphous solid prepared from bones and consists principally of tricalcium phosphate and carbon. It should not be confused with bone meal, which is derived from the same source but by a different treatment and consists of tricalcium phosphate and organic matter; nor with "spent" bone black which is a bone black that has been recovered following its use in any one of several industrial processes.

The virgin bone black under test showed high porosity and physical stability, both desirable properties, evident in the low loss from attrition and in the long

life of the filter bed. The virgin bone black used in the tests was 30-40 mesh granules, manufactured by Consolidated Chemical Industries, Inc. of Houston, Texas, and at the time the tests were made could be purchased through Oklahoma jobbers, packed in 100 pound bags at 7 to 10 cents per pound, depending upon the quantity purchased.

COMPARATIVE TESTS ON FLUORIDE REMOVAL

Table II

Analyses of waters used in the tests

Water (a) Certain water- the cause of this investigation		Water (b) Tulsa City water. Used in comparative tests
471.4 p.p.m.	Na-K (as Na)	4.7 p.p.m.
2.8 "	Ca	30.0 "
1.0 "	Mg	1.3 "
187.7 "	SO ₄	7.3 "
890.6 "	HCO ₃	93.0 "
nil	CO ₃	nil
87.7 "	Cl	4.5 "
3.4 "	F	less than 0.05 "
1,638.6 "	Total solids	140.8 "
0.65 grs.	Total hardness. Gr/Gal. CaCO ₃	4.7 grs.
29.52%	Primary Salinity	11.04%
nil	Secondary Salinity	4.42%
69.42%	Primary Alkalinity	nil
1.06%	Secondary Alkalinity	84.52%
8.0	pH Value	7.6

(1) Laboratory tests were made, using 10-pound filter beds and Water (b), Table II (Tulsa City Water) to which had been added sodium fluoride in an amount to give the water a fluoride content of approximately 5 parts per million. Naturally, the least fluoride will be found in the first effluent water but will gradually increase as the filter medium becomes more and more saturated with the absorbed fluorides, and subsequently less efficient.

The results given in Table III indicate that virgin bone black has a high fluoride-absorption capacity on water of this type.

TABLE III
COMPARATIVE TESTS ON FLUORIDE REMOVAL
Based upon water (b), Table II plus sodium fluoride

Filter Medium	Average rate of flow gals per hr.	Vol. of water in gallons passed through before effluent water shows fluoride increase to 1 p.p.m.	Fluoride content of effluent water. Average for total treated water.
Special Calcium Phosphate	7.2	320	0.70
Processed Bone Meal	3.3	703	0.90
Virgin Bone Black	4.0	790	0.25
Virgin Bone Black	18.3	780	0.58
Virgin Bone Black	20.0	770	0.55

(2) Comparative field tests were made on water (a), Table II, using 100-pound filter beds, one containing virgin bone black and the other special calcium phosphate material. On these tests the rate of filtration was adjusted to a maximum of 90 gallons per hour. The treatment was controlled by automatic-level valve in the water supply tank. The average rate of filtration was 180 gallons per day through the 100-pound filter bed. Results are given in Table IV. The virgin bone black showed greater absorption capacity and much lower cost than the special calcium phosphate material.

TABLE IV
RESULTS OF FIELD TESTS ON FLUORIDE REMOVAL

Filter Medium	Cost of filter bed	Volume of filtered water	Fluoride content of final effluent.
Special Calcium Phosphate	\$28.00	3,780 gals.	1.1 p.p.m.
Virgin bone black	\$ 7.50	4,140 gals.	1.0 p.p.m.

INFLUENCE OF pH ON FLUORIDE REMOVAL

A series of comparative tests were conducted on removal of fluorides with special calcium phosphate material, regenerated special calcium phosphate material, virgin bone black, and regenerated virgin bone black using Water (a), Table II which contains 900 parts per million bicarbonates, practically all in the form of sodium bicarbonate. A second series was run identical

with the first in every respect except that the bicarbonate content had been reduced to 100 parts per million through addition of hydrochloric acid. (Conversion of part of the sodium bicarbonate to sodium chloride). Every one of the filter materials showed increased efficiency of better than 200 percent following lowering of the bicarbonate content. These tests indicate that it may be advisable to correct the pH value on highly alkaline waters before attempting to remove the fluorides.

RATE OF FLOW OF WATER THROUGH FILTERS

The removal of fluorides by virgin bone black may be influenced by the presence of dissolved matter such as salts of iron and aluminum, by the hardness of the water, by the alkalinity of the water, by suspended matter (silt), by algae and other organic growth, by the size granulations of the bone black, and by the rate of flow of the water through the filter. The optimum rate of flow will depend upon the other factors given. Accordingly, in calculating size and capacity for new installations for fluoride removal, ample leeway should be allowed for fluctuations. A flow rate of 2 gallons per hour for each 10 pounds of filter medium in the filter bed should yield satisfactory results on any water suitable for human consumption. A higher flow rate of 4 gallons per hour for each 10 pounds of filter material has given good results with any water encountered in this investigation. If the water contains silt or organic matter, it may have a detrimental effect on the filter bed which would warrant preliminary filtration for their removal.

REGENERATION OF FILTER MATERIAL

The caustic soda-carbon dioxide regeneration method, recommended for the special calcium phosphate material, may be satisfactory in connection with most of the large installations, but the very nature of caustic soda and carbon dioxide necessitates especially designed equipment, and requires such close care and attention in handling as is to be had only with skilled operators. Such requirements are too expensive for small installations and can be obviated to some degree by the use of other regenerative reagents.

In this investigation excellent regeneration of the virgin bone black was obtained by using trisodium phosphate in place of caustic soda, and sodium acid phosphate (monosodium phosphate) in place of carbon dioxide. Both materials are obtainable through chemical dealers and are relatively non-corrosive, safe, and easy to handle. Table V compares results of the two regeneration methods on virgin bone black. The water used was Water (a), Table II—a high sodium bicarbonate water fortified to 30 parts per million fluorides by addition of sodium fluoride. However, hydrochloric acid was substituted for carbon dioxide, as in the older directions. The substitution was made because the hydrochloric acid was readily available and the carbon dioxide was not, and because a similar situation would exist if the process were attempted for small installations. The relatively higher cost of trisodium phosphate and sodium acid phosphate over caustic soda and either carbon dioxide or hydrochloric acid is more than compensated for by the considerations mentioned.

TABLE V
COMPARATIVE TESTS ON REGENERATION METHODS

10-pound virgin bone black filter bed.			
Method of regeneration.	Gallons of water through original filter bed before fluorides increased to 1 ppm.	regenerated filter bed before fluorides increased to 1 ppm.	Percent efficiency of regeneration.
(1) Treat with 10.5 gals. 2.2% trisodium phosphate solution. Wash with 28.4 gals. fluoride-free water.	83.6	88	88.1
Follow with 15.8 gals. 1% sodium acid phosphate solution. Wash with 28.4 gals. fluoride-free water.			
(2) Treat with 4 gals. 1% caustic soda solution. Wash with 20.0 gals. fluoride-free water.	83.6	45	70.8
Follow with 3 gals. 0.7% hydrochloric acid solution. Wash with 20 gals. fluoride-free water.			

In an experimental filter installation special calcium phosphate material had been used. Repeated attempts to regenerate the filter bed resulted in comparative failure. It is possible and very probable that the

unsatisfactory regeneration in this case was due to the high sodium bicarbonate content of the water. (Water (a), Table II). However, regeneration of virgin bone black used on this same water was shown by repeated laboratory tests to be fairly satisfactory. At small field installations it has been found more practical to discard the spent filter material rather than to use any method of regeneration.

ODOR AND TASTE REMOVAL

During the tests on water (a), Table II, it was noted that the water as it came from the well had an appreciable odor and taste, probably due to minute amounts of dissolved natural gas. This odor and taste was removed by contact with the virgin bone black, but not by contact with the special calcium phosphate material, indicating that odor and taste absorption by the carbon of the virgin bone black may be the explanation."

CONTROL OF FILTERS

Satisfactory fluoride removal will result only through knowledge and control of the condition of the filter bed. When the efficiency of the filter medium has declined so that the fluoride content of the effluent water has risen to 1 part per million, the filter should be changed, or regenerated. Determination of the fluoride content of water is best made by following the procedure recommended by the American Water Works Association.²³ However, a modified procedure may be followed which will give a practical approximation under most conditions. The modification lies mainly in control of the pH value and in preparation of the standards from the water which is to be tested but from which all fluorides have been removed. Thus, the impurities which may exert an influence on the determination are the same in both the standards and the water under test.

Equipment needed:

- 1 -Erlenmeyer flask, 250 ml. capacity.
- 3 -Pipettes. 5ml. capacity. Calibrated to 0.1 ml.
- 6 -Nessler tubes. Calibrated at 100 ml.
- 1 -Glass rod for agitation in tubes.
- 2 -Glass bottles. 1 gal. size.
- 1 -Filter funnel. (glass) 90 mm. dia.
- 1 -Graduated cylinder. 100 ml. capacity. Cali-

brated to 1 ml.

1 -pkg. Filter paper. No. 30. 15 cm. dia.

Solutions required:

- (1) Hydrochloric acid solution. 0.3 normal.
- (2) Fluoride solution. Dissolve 0.221 gms. Sodium Fluoride in 1 liter distilled water. Each milliliter will contain 0.1 milligram fluoride.
- (3) Methyl Red Indicator. Dissolve 0.1 gm. Methyl Red crystals in 100 mls. 60% alcohol.
- (4) Alizarin Reagent. Dissolve 0.17 gm. alizarin sodium sulfonate in 100 mls. distilled water, and 0.87 gm. zirconium nitrate crystals in 100 mls. distilled water. Mix the two solutions. Shake at intervals and let stand over night before using. Store in amber bottle in cool, dark place. When ready to use, dilute 5 mls. to 100 mls. with distilled water.
- (5) Water for Standards. Nearly fill a gallon bottle with water from the system. Add sufficient virgin bone black to the water to remove all fluorides. Four tablespoonfuls will be ample on most waters, but on water containing 10 to 12 parts per million fluorides together with high concentration of sodium bicarbonate, it may be necessary to use as much as three quarters of a pound. Shake occasionally for several hours and allow to stand overnight. Filter carefully. Store the filtered water in clean bottles.

Equipment and solutions other than "water for standards" may be obtained from commercial laboratories or chemical supply houses. The method of procedure in determining the fluoride content of water coming through the filter follows:

- (1) Determine the amount of 0.3 normal hydrochloric acid solution necessary to neutralize exactly 100 mls. "water for standards" and also the water to be tested. Use a Nessler tube for measuring. Place the water in an Erlenmeyer flask, and add 2 drops Methyl Red indicator. Then add hydrochloric acid solution drop by drop from a pipette and with agitation until the color changes from yellow to clear red. Note the exact amount used.

(2)

Place six Nessler tubes in a holder. Number them from 1 to 6. Tubes 1 to 5 inclusive are filled to the 100 ml. mark with "water for standards", and tube 6 with water to be tested. Add to each tube the amount of hydrochloric acid solution required for neutralization plus exactly 2.0 mls. excess.

(3)

Add fluoride solution to tubes as follows: tube 1 -- 0.0 ml.; tube 2 -- 0.5 ml.; tube 3 - 0.75 ml.; tube 4 - 1.0 ml.; and tube 5 - 1.25 mls. Thoroughly mix the contents of each tube.

(4)

Add exactly 1.0 ml. diluted alizarin reagent to each of the six tubes. Again, thoroughly mix contents of each tube.

(5)

After standing for 1 hour, examine and compare tube 6 with the others. The red color will be bleached out in proportion to the amount of fluorides present. Since tubes 2, 3, 4 and 5 contain 0.05, 0.75, 0.10 and 0.125 mls. fluorides respectively in 100 gms., they represent 0.50, 0.75, 1.00 and 1.25 parts per million. If the fluoride content of tube 6 appears to be 1.0 p.p.m. or greater, the filter material should be replaced with fresh material, or subjected to regeneration.

FLUORIDE REMOVAL INSTALLATIONS

Virgin bone black has been in use more than four years in installations at three small water supply systems on leases of a major oil company. The results have been highly satisfactory. One of the systems has a filter holding 100 pounds of virgin bone black, and the other two hold 200 pounds each. The filters (or treaters) were constructed in accordance with the design shown in Figure 2, and can be constructed easily in any machine shop from material usually obtainable in every community. No protective coating against corrosion in the treater is necessary. The 200-pound capacity treaters were constructed at a cost of \$40.00 each.

Such treaters should prove suitable for installations in small communities, oil-field camps, in rural schools, etc., wherever large commercial installations are impossible or impractical. For individual homes and

small schools it should be possible to utilize the principle of fluoride removal with virgin bone black in some inexpensive manner, the exact details of which will depend upon the type and source of the water supply, but not beyond the resources and ingenuity of the average person.

Case and Goodnight used a field-test outfit of 15-pounds virgin bone black capacity which worked very well. A sketch is given in Figure 3.

It is suggested that a 5-gallon glass water bottle be used to hold the filter medium through which the water could be passed for fluoride removal. Also, a 5-gallon glass water bottle might be used as a raw water reservoir, and be connected to the bottle containing the filter medium. In any event the efficiency of such a treater will depend upon proper contact of the water with the filter medium for the necessary length of time for fluoride absorption to take place. Figure 4 gives sketch of a possible treater installation for small consumers.

CONCLUSIONS

From a consideration of the foregoing facts and figures, it seems apparent that it should be practical to utilize virgin bone black for the removal of fluorides from drinking water for the individual home and for small communities where the standard commercial treating plants are not warranted; and that the fluoride content can be reduced to a point safe to the health of the consumer at a cost of only a fraction of a cent per gallon for any water so far examined and without recourse to any method of regeneration, discarding the bone black whenever it has lost its fluoride absorption power. Regeneration by backwashing with trisodium phosphate may be justified on some larger installations but it is not recommended for the small ones.

Sketches of inexpensive treaters are shown to assist interested persons in planning systems suitable for their individual requirements.

The first consideration should be to determine whether or not the water is satisfactory for human consumption. The Oklahoma State Health Department at Oklahoma City is ready to cooperate in this matter. When

it is known that the water is satisfactory except for excessive amounts of fluorides, there may still be variations in the composition of the water which render impractical any hard and fast rules for treating procedure. The efficiency of the filter medium may be influenced by suspended matter, by algae and other organic growth, by the degree of hardness of the water, by the degree of alkalinity, and by the presence of dissolved matter such as iron and aluminum salts. A complete analysis of the water should be made to determine the presence of any chemical or substance which will interfere with the removal of fluorides.

The second consideration should be the probable maximum daily consumption and the probable peak short-period consumption, from which may be calculated the size and capacity of a system to supply the needs of the people to be served, bearing in mind that the thickness of the filter bed, and the grain size of the bone black influence the rate at which water may be passed through with satisfactory removal of the fluorides. Also, it should be recognized that an undersized filter may be forced beyond its absorption capacity by heavy withdrawals, but an oversized filter will have a good margin of safety in such emergencies. It is recommended that the calculations be based upon a flow rate of 2 gallons per hour for each 10 pounds of filter bed. A much faster flow rate may be found to yield good results, but until laboratory tests or other experimentation has proven the faster rate feasible it is better to figure on the slower rate.

The quantity of water which was treated per pound of virgin bone black may be computed from Tables III and IV. It will be observed that on water (a) Table II, 1 pound of virgin bone black removed 2.4 p.p.m. fluorides from 41.4 gallons, equivalent to the removal of 1 p.p.m. from 99.4 gallons; whereas on water (b) Table II, 1 pound of virgin bone black removed 4.0 p.p.m. fluorides from 76 gallons, equivalent to the removal of 1 p.p.m. from 304 gallons. It is evident that the bone black is three times as efficient on water (b) as on water (a). However, for any given water it is probable that the quantity of water which can be treated will

be in direct proportion to the fluoride content. In other words, if water (a) contained 2 p.p.m. fluorides and 1 pound of virgin bone black reduced the fluoride content to 1 p.p.m. in 100 gallons, it is reasonable to expect that if this water had contained 11 p.p.m. fluorides originally, then 1 pound of virgin bone black would reduce the fluoride content to 1 p.p.m. in 10 gallons.

Where a water contains excessive amounts of fluorides (6 p.p.m. or more), together with a heavy concentration of sodium bicarbonate, consideration should be given to the advantage to be derived from preliminary treatment to reduce the pH value and to convert the sodium bicarbonate into a less objectionable compound.

After a system has been designed, built, and placed in operation, periodic tests should be made to determine when replacement or regeneration of the filter material is necessary. A simplified test is given under the heading Control of Filters which should prove practical under most conditions.

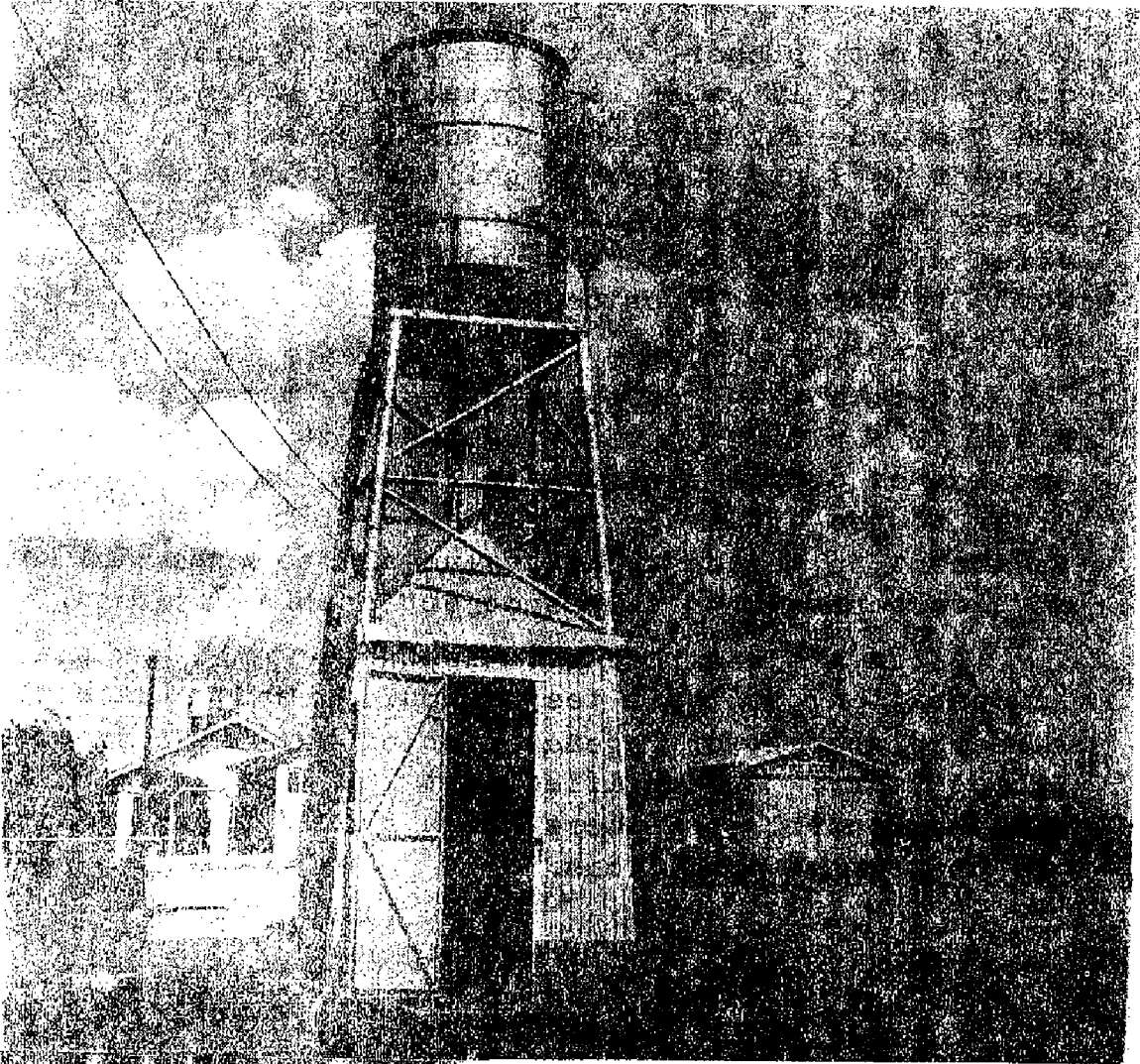
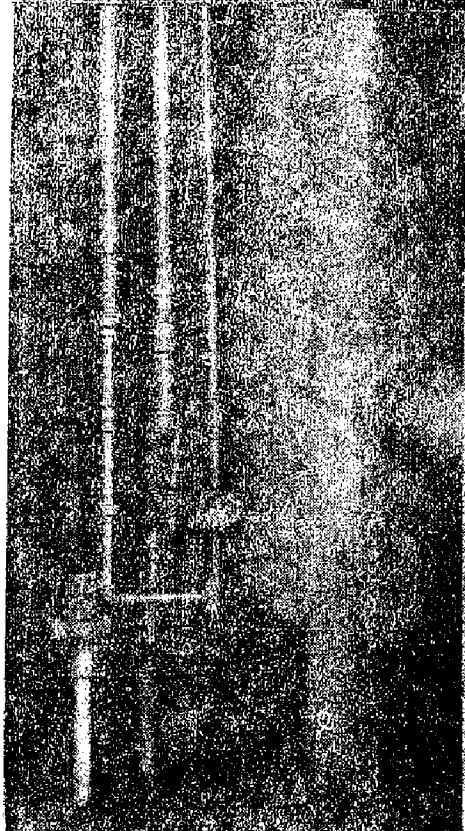


PLATE 1

EXTERIOR VIEW

Fluoride-Removal Installation
at an oil-field camp.



INTERIOR VIEW

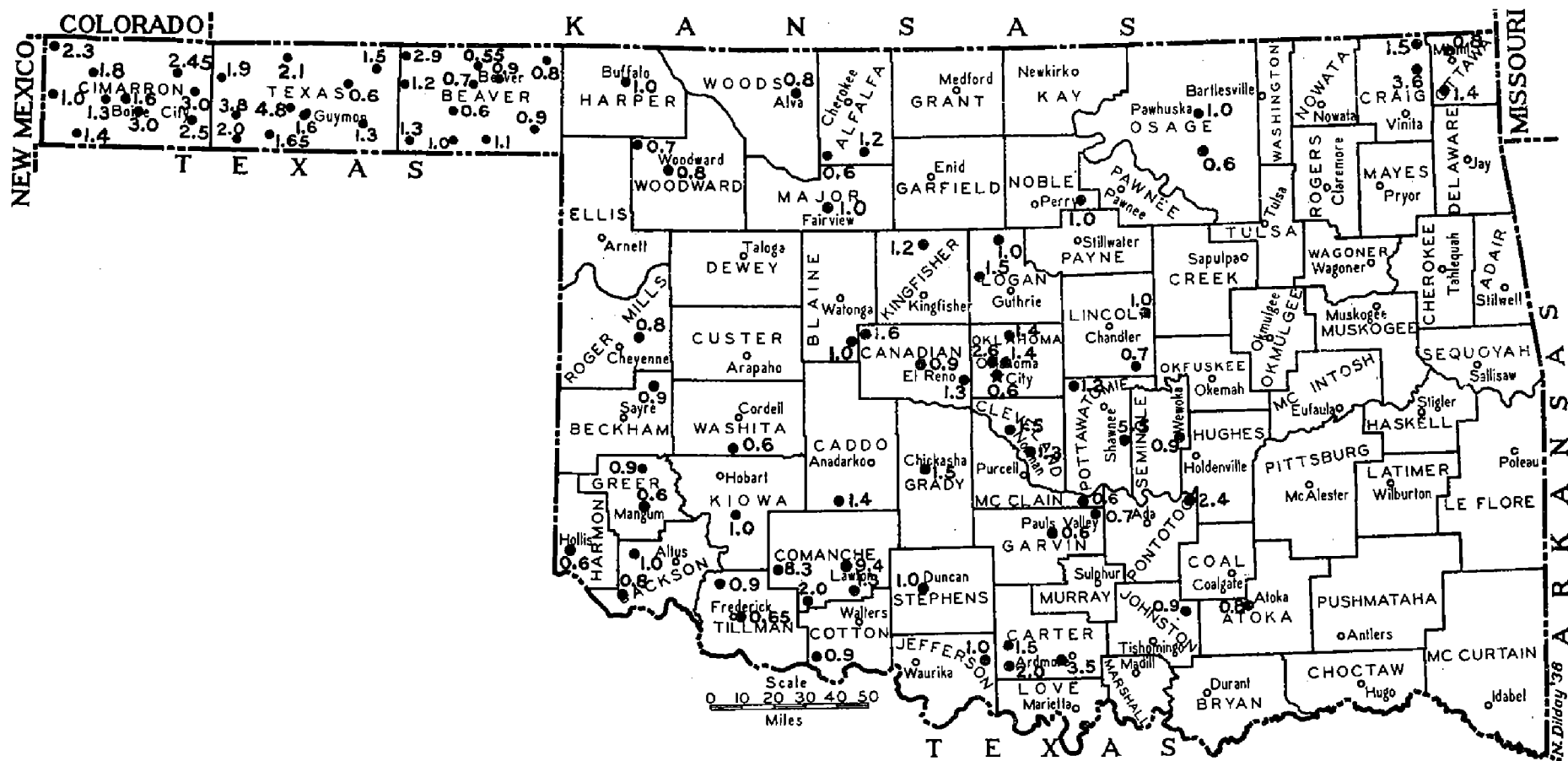
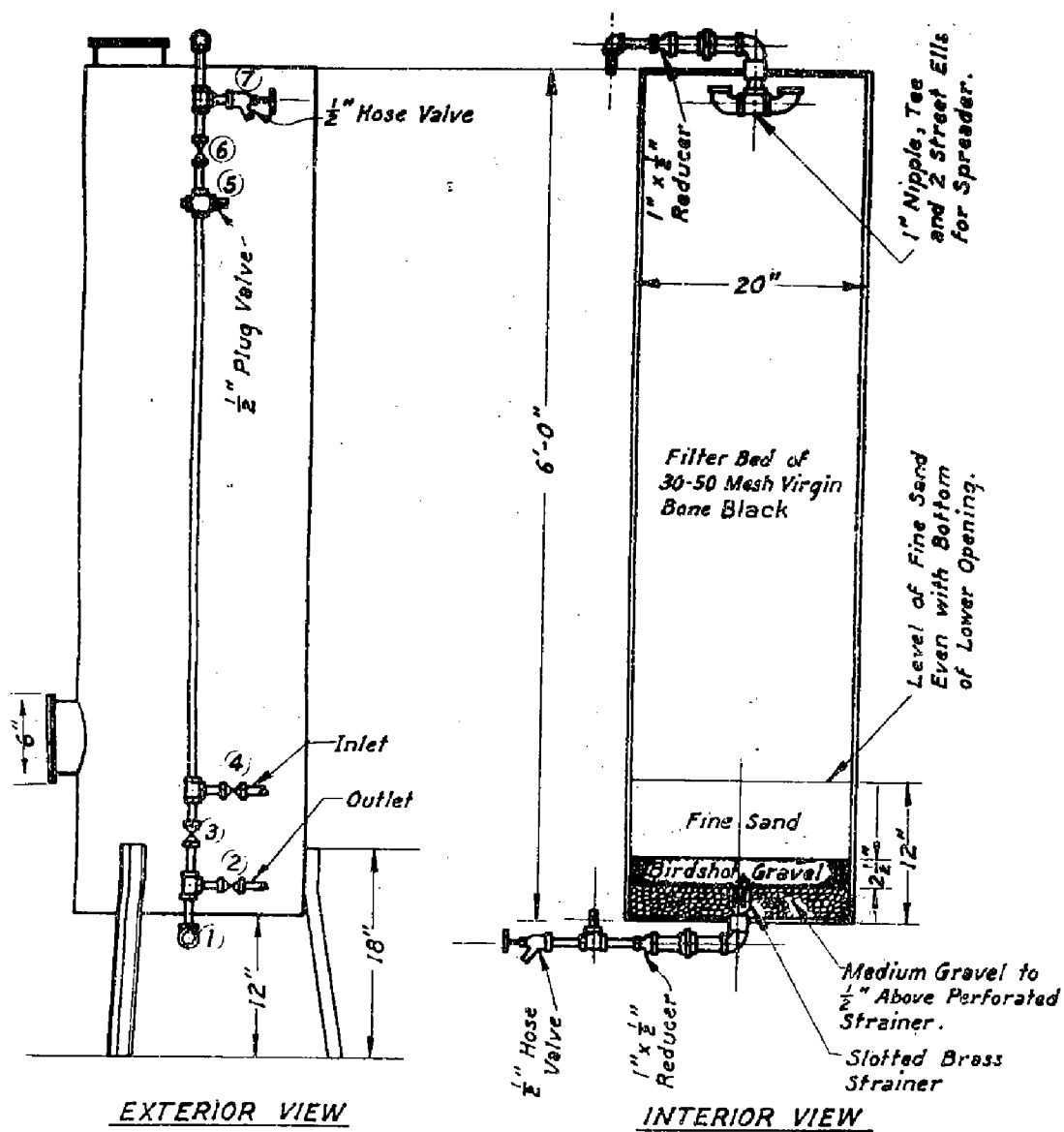


FIGURE 1
Index Map of Oklahoma showing general distribution of known fluoride waters



PIPE WORK AND FILTER BED CONSTRUCTION ON FLUORIDE REMOVAL FILTER

FIGURE 2

Sketch showing structural details of fluoride removal filter.

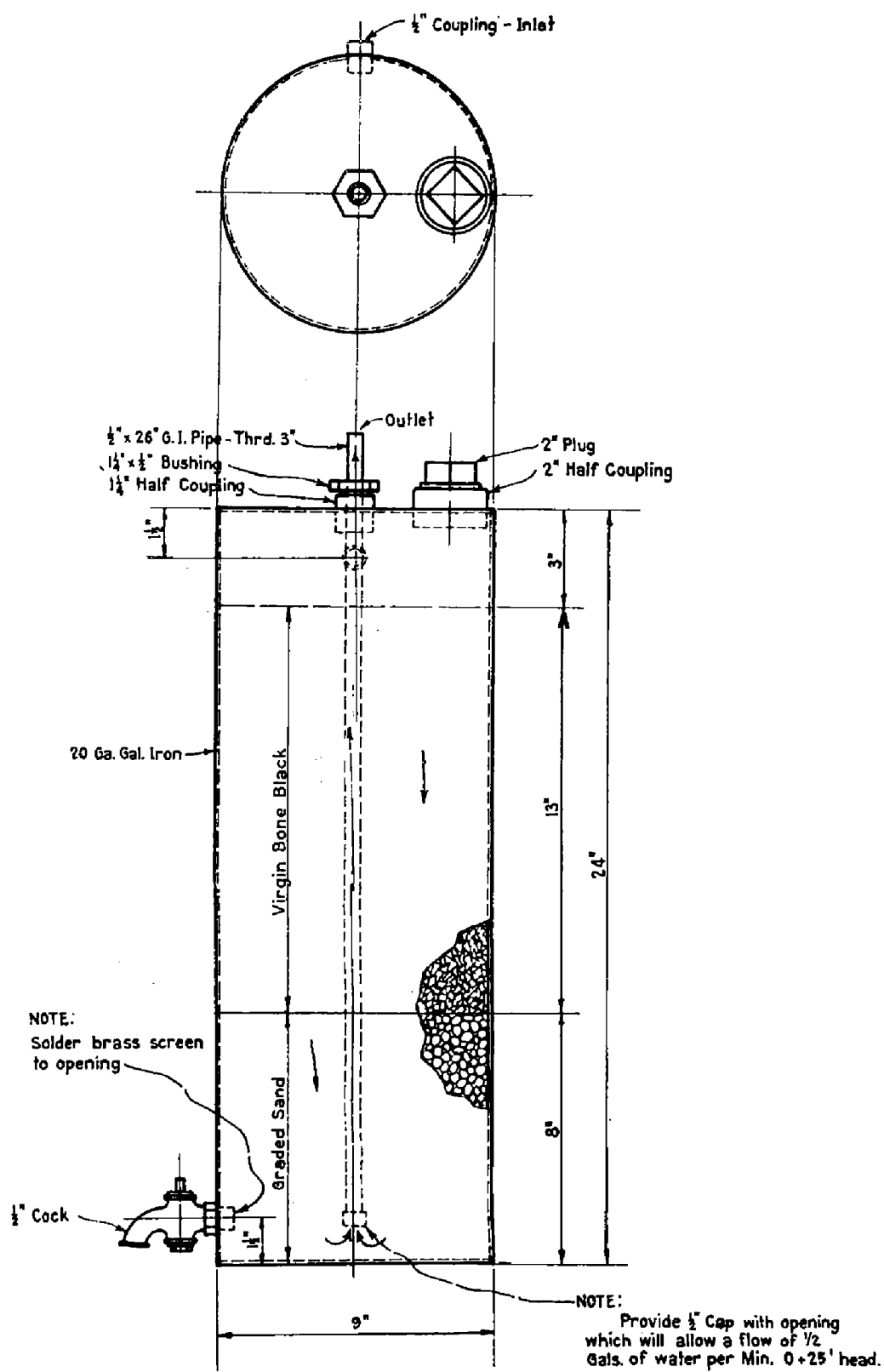


FIGURE 3
 Sketch of portable field test unit for fluoride removal.

A SMALL FLUORIDE REMOVAL FILTER UNIT

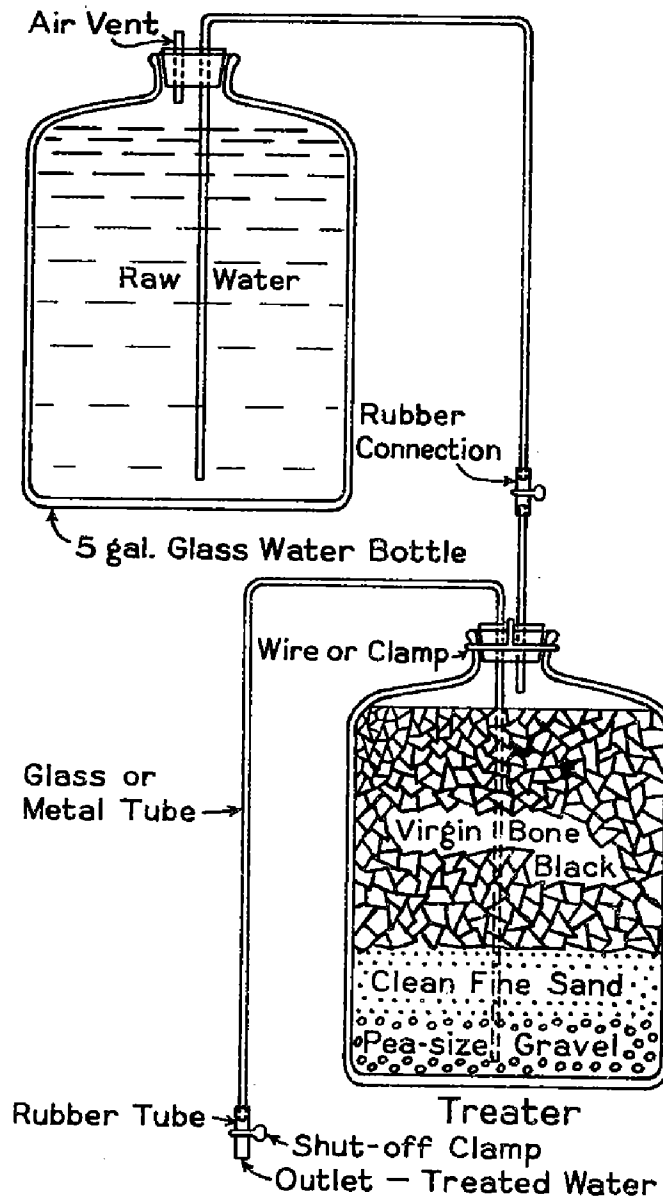


Figure 4.

INSTRUCTIONS

Pea-sized washed gravel is placed in a 5-gallon glass water bottle to a depth of 2 inches; then 2 inches of clean fine sand is placed on top of the gravel. On top of sand add virgin bone black (30-40 mesh) to fill the bottle. Introduce the stopper and glass tube intake and outlet assembly. Wire or clamp the stopper in place, securely enough to withstand the pressure exerted by the intake water. Connect to the water supply and regulate the flow to a point below that at which the filter material is disturbed. The treater is then ready to operate.

When running water is not available, a second 5-gallon glass water bottle may be filled from the well, spring or other source of supply and connected at sufficient height above the treater to give the necessary head. The water from this second bottle may be drained from an inverted position as in the usual bottle-water dispenser, or the bottle may be upright and drain by means of a siphon.

REFERENCES

- (1) Smith, H.V., (and others), Ariz. Exp. ~~Engineering~~ Cation, Tech.
- (2) Kehoe, Robert A.; Cholak, Jacob.; Large ~~Engineering~~ nt, Edward J
Works Jour. Vol. 36, No. 6, 1944, pp ~~845-847~~ 845-87.
- (3) Public Health Service Drinking Water S ~~Standards~~ Standards. U. S.
ports. Vol. 58, 1943, p. 89.
- (4) Ast, D.B., U.S. Pub. Health Reports. VO ~~1~~ 58, No. 2
- (5) Dean, H. T., Amer. Water Works Jour. VO ~~1~~ 35, No. 9
- (6) Boruff, C.S., Ind. & Eng. Chem. Vol. 28 ~~1~~ No. 1, 1934,
- (7) Fink, C.K.; Lindsay, F.K., Ind. & Eng. ~~Chem.~~ Chem. Vol. 28
pp. 847-8.
- (8) Churchill, H.V., U.S. Patent. 2,059,552 ~~1~~
- (9) McKee, R.H.; Johnston, W.S., Ind. & Eng ~~Chem.~~ Chem. Vol.
pp 849-51.
- (10) McKee, R.H.,: Johnston, W.S., U.S. Patent ~~2,072,376~~ 2,072,376
- (11) Smith, H.V.; Smith, M.C., Water Works ~~Engineering~~ Engineering.
- (12) Smith, H.V., (and others); Ariz. Exp. S ~~Engineering~~ Cation. Tech.
- (13) Elvove, E., U.S. Public Health Reports. ~~1937-1938~~ 1937-1938.
- (14) MacIntire, W.H.; Hammond, J.W., Ind. & ~~Engineering~~ Eng. Chem. V
1938, pp 180-2.
- (15) MacIntire; U.S. patent. 2,128,793. Aug- ~~16, 1938~~ 16, 1938.
- (16) Adler, Howard; Klein, George; Lindsay, ~~1938~~ F.K.,: Ind. &
30, No. 2, 1938. pp 183-5.
- (17) Behrman, A.S.; Gustafson, H.; Ind. & En ~~Chem.~~ Chem. Vol.
1938, pp 1011-13.
- (18) Behrman & Gustafson.; U.S. Patent. 2,227 ~~432~~ 432. Jan. 7,
International Filter Co.)
- (19) Goetz, Paul C.; U.S. Patent. 2,139,227. ~~Dec. 6, 1938~~ Dec. 6, 1938
- (20) Elvove, Elias.; U.S. Patents. 2,207,725 ~~July 1940~~ July 1940;
1941. (to U.S. Gov't.)
- (21) Sanchis, J.M.; Ind. & Eng. Chem. Anal. ~~1933~~ dit. Vol. 6,
pp 134-5.
- (22) Willard, H.H.; Winter, O.B.; Ind. & Eng ~~Chem Anal.~~ Chem Anal.
No. 1, 1933, pp 7-10.
- (23) Committee Report. Amer. Water Works Jou ~~1965-2017~~ Vol. 33,
pp 1965-2017.