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FLUORIDE REMOVAL FROM POTABLE WATER SUPPLIES

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F I N A L R E P O R T

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ABSTRACT

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The objective of this project was to determine whether or not the fluoride level in waters with moderate fluoride content (2 to 10 mg/l) could be reduced to acceptable levels by chemical treatment. The optimum concentration for dental health is from 1.1 to 1.8 mg/l. A variety of methods for the removal of fluoride have been reported in the literature.

In this study, we compared the methods which appeared to have some possibility of success. Coagulation with alum at pH levels of 6.2 to 6.4 was one of the more effective methods tested. Fluoride was also found to be adsorbed by magnesium hydroxide. This occurs in the softening process with magnesium-containing waters, and could be increased by adding both magnesium salts and lime. The formation of fluorapatite by the reaction of fluoride with phosphoric acid and lime was found to be very effective for the removal of fluoride. Flocculation with iron salts was found to be of little benefit in the removal of fluoride. The fluoride removed was from 2 to 10 percent of the initial concentration. Activated charcoal was tested without any appreciable success. Polyelectrolytes, in general, did not remove fluoride, but were very helpful in obtaining good clarification for some processes and thereby aided in fluoride removal.

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INTRODUCTION

Natural waters contain fluorides in varying amounts. Consumption of water that contains fluoride in a concentration of approximately 1 mg/liter has been found to be effective in reducing tooth decay. For this reason fluoride compounds are usually added to water supplies which contain less than the desired concentration. In communities where the fluoride content in the water supply is at an optimum level, tooth decay has been shown to be almost 65% less than in communities with little or no fluoride in the water. Most unfluoridated waters contain less than 0.3 mg/l fluoride.

Excessive exposure to fluoride, however, may cause fluorosis, a condition in which the teeth become mottled, discolored, and pitted during their development (1). Skeletal fluorosis, characterized by increased bone density and abnormal bone growths, may result from long-term consumption of water containing 8 to 20 mg/l of fluoride (2). The consumption of fluorides in excess of 20 mg/day over a period of 20 years or more could result in crippling fluorosis (3).

Although dental health is probably of primary consideration for the control of fluoride in water, the more severe effects of excessive levels make it necessary to reduce the amount of fluoride present. The USEPA National Interim Primary Drinking Water Standards have indicated that the allowable level of fluoride should not exceed 1.4 to 2.4 mg/l. This level is dependent upon the average maximum daily air temperature since the amount of water, and consequently the amount of fluoride ingested, is primarily influenced by the air temperature of the area. In general, most municipal water supplies contain less fluoride than the amount that

is considered to be beneficial to dental health; however, many water supplies are found that exceed this limit. In the State of Illinois, for example, a study which considered 129 water supplies that exceeded the new federal drinking water standards indicated that the fluoride levels ranged from 1.6 to 8.0 mg/l with approximately 50% of these levels in excess of 2.2 mg/l. In addition, there are a number of scattered sites throughout the state that have fluoride levels in excess of 8 mg/l.

In 1974 the EPA reported that approximately 1200 municipal water supplies in the United States had fluoride levels considerably in excess of the 1962 PHS drinking water standards (4). Concern about elevated fluoride levels in drinking water is not based so much on acute toxicity effects, but rather on the long-term exposure to low levels of fluoride.

A number of investigations have been made on a variety of treatment methods for the removal of fluoride from potable water supplies. Reviews of these methods have been presented by Sorg (5), Link and Rabosky (6), Savinelli and Black (7), and Maier (8). A technical manual which compares the effectiveness and cost of water treatment processes for the removal of specific contaminants has been published by the USEPA (4). The methods for fluoride removal that have been tried or proposed have been divided into two basic groups, (a) precipitation methods based upon the addition of chemicals to the water during the coagulation or softening processes and (b) methods in which the fluoride is removed by adsorption or ion exchange on a medium which can be regenerated and reused. The activated alumina column is a noteworthy example of this latter group.

The primary objective of this project was to determine whether or not the fluoride level in potable water supplies with a moderate fluoride content could be reduced to an acceptable level by chemical treatment.

A second objective of this project was to screen the methods available and to determine the most advantageous method for reducing fluoride at various natural levels.

Emphasis, in this study, was placed upon precipitation methods in which the treatment chemicals were added to the test water for the formation of fluoride precipitates, or the adsorption of fluoride upon the precipitates formed.

This study was not intended to investigate the removal of fluoride from potable water by column adsorption. However, these methods should be mentioned since they are in current use and appear to be the most effective methods available for water supplies with fluoride concentrations of 5 to 10 mg/l. The adsorbents that have been used are activated alumina, bone char, and tricalcium phosphate. Of these, activated alumina has been the most successful, and it is presently being used in 3 large defluoridation plants in the west. The use of activated alumina in the Bartlett, Texas, defluoridation operation proved its effectiveness for fluoride removal for over a 25-year period. Bone char has also been used as an effective adsorbent, but difficulties have been experienced with waters that contain both fluoride and arsenic (9). Losses of the bone char occur during its use and regeneration due to its solubility in acid. Thus, more carefully controlled conditions are required for this adsorbent.

EXPERIMENTAL DETAILS

A synthetic test water was used in the majority of these tests and was referred to as the "standard test water." This was prepared with the following composition:

	<u>mg/l</u>
NaHCO ₃	168.0
CaCl ₂ ·2H ₂ O	40.0 (as Ca ⁺⁺)
MgCl ₂ ·6H ₂ O	24.3 (as Mg ⁺⁺)
NaF	2-6 (as F ⁻)
Water to a liter	

Reagent grade chemicals and deionized water were used in the preparation of all solutions.

In a few tests the local tap water with added fluoride was used.

This is a lime softened water with the following composition:

	<u>mg/l</u>		<u>mg/l</u>
Calcium	13.6	Phosphate	0.0
Magnesium	11.7	Silica	6.8
Strontium	0.13	Fluoride	1.1
Sodium	32.9	Boron	0.3
Potassium	2.6	Chloride	5.0
Ammonium	0.9	Sulfate	34.1
Barium	<0.1	P Alkalinity (as CaCO ₃)	12.0
		M Alkalinity (as CaCO ₃)	117.0
		Hardness (as CaCO ₃)	82.0

Equipment

1 - A Beckman research model pH meter, equipped with a Beckman #39000 research GP glass electrode and a Beckman #39071 frit-junction calomel (with sidearm) reference electrode, was used to measure the pH of the solutions. The relative accuracy of the meter is specified by the manufacturer to be ±0.001 pH.

2 - A six-place multiple stirrer (Phipps and Byrd, Richmond, Virginia) was used for uniform stirring of the solutions in the coagulation studies. The unit is equipped with conventional 1 × 3 inch paddles and a tachometer for measurement of the stirring rate. The base unit which supports the test beakers provides illumination for floc detection.

3 - Fluoride analyses were made using a specific ion combination electrode, Orion model 96-09-00, and an Orion specific ion meter, model 401. TISAB II buffer was used to maintain the proper pH of the test solutions and eliminate the effects of the complexing ions.

Procedures

1 - In the coagulation studies, aliquots of the standard test water in approximately 1-liter volumes were poured into beakers and placed on the 6-place multiple stirrer for agitation during chemical additions. Initial pH readings and additions of chemical constituents were made with mixing at 20 rpm. Predetermined amounts of the chemical coagulants were added to the beakers with rapid mixing at 100 rpm over a period of 1 to 5 minutes, or as otherwise specified. The additions of polyelectrolytes as flocculant aids in some tests were made at different times and are described in these tests. The stirring speed during flocculation was reduced to 20 rpm for a period that ranged from 0.5 to 1.0 hour. The stirrer was then stopped and the flocs permitted to settle. The settling rates of the flocs varied considerably with the individual tests; however, a minimum period of 0.5 hour was allowed before analyses were made on the clarified samples.

2 - In the activated alumina adsorption tests, a column 18 mm in diameter and 12.5 cm high was prepared in the following manner: A 25 g

quantity of activated alumina (48 mesh - 100 mesh, washed free of fines) was rinsed into the column with tap water. The column was backwashed with tap water at 100 percent expansion for a 15-minute period after which the column bed was settled and the water drained to the top of the bed.

A 100 ml volume of a 1.0 percent solution of sodium hydroxide was then passed through the column at a rate of 7-10 ml/min. The column was then rinsed with 400 ml of deionized water at a rate of 7-10 ml/min. Excess caustic was neutralized with 100 ml of 0.10 N sulfuric acid, which was followed by a 100 ml rinse with deionized water. The column was then ready to proceed with the fluoride exchange cycle. The test water was passed through the column at a rate of 15 to 20 ml/min until the fluoride equivalent in the effluent reached 1.0 mg/l. The total effluent was collected and representative samples were analyzed for fluoride, alkalinity, and pH. At the end of the exchange cycle the column was regenerated and the regenerant effluents were collected for analysis.

3 - In the determination of fluoride, 50 mls of Total Ionic-Strength Adjustment Buffer (TISAB II) were added to an equal amount of test water, or to a dilution made up to that volume. The combined solutions were placed on a magnetic stirrer for uniform mixing, the combination electrode immersed, and after a 3-minute period the fluoride concentration was read directly from the meter. The meter was calibrated against a fluoride standard of 1.0 mg/l before taking the fluoride readings and the calibration checked after every five measurements using the fluoride standard.

4 - Other analyses were made using procedures outlined in the 14th edition of "Standard Methods for the Examination of Water and Wastewater" (10).

RESULTS

Coagulation with Alum

Fluoride removal by coagulation with alum appears to be an adsorption process in which the fluoride ions are removed along with the flocculated materials in the sedimentation step of the process. The efficiency of fluoride removal by this process is dependent upon the initial fluoride concentration, the alum dosage applied, and the pH at which the flocculation occurs. Boruff (11) investigated the use of a number of materials for the removal of fluoride from potable water, and was the first to attempt the removal of fluoride by alum coagulation. Kempf (12) and later Scott et al. (13) reported on the removal of fluoride from well water by alum coagulation. Culp and Stoltenberg (14) observed that the fluoride level in the LaCrosse, Kansas, drinking water was reduced from an initial concentration of 3.6 to 1.8 mg/l by an alum dosage of 200 mg/l. Incremental feeding of the alum during the rapid mix period was found to reduce the alum requirement by approximately 10 percent, when compared with the normal method of single addition. A number of studies have indicated that fluoride removal by alum coagulation is a function of pH and the optimum pH reported for fluoride removal is in the range of 6.0 to 7.5 (14,15,16). Culp and Stoltenberg (14) also studied the effect of pH on fluoride removal from the LaCrosse drinking water by alum coagulation over a pH range of 5.0 to 10.5. They reported an optimum pH of 6.5 for maximum fluoride removal. They also noted that this pH offered an added advantage in that the solubility of aluminum is at a minimum at pH 6.5 and, therefore, would not become a problem in water systems.

On the basis of their observations in this study the removal of fluoride by the method of alum flocculation was recommended over the activated alumina process.

To determine the optimum pH for fluoride removal in our initial jar tests, aliquots of standard test water were adjusted to pH levels within the optimum range of 6.0 to 7.5, flocculated with several dosages of alum, and the reduction in the concentrations of fluoride determined. Analyses for fluoride were made on the clarified solutions after sedimentation of the floc. The pH values in these tests were obtained by bubbling carbon dioxide through the solutions prior to the addition of alum. The results of these tests shown in Table 1 indicated the optimum pH level to be in the range of 6.2 to 6.4.

In some 30 to 40 jar tests that followed, fluoride removals by various dosages of alum were determined using a slightly modified test water to which calcium had been added in concentrations of 50 and 200 mg/l. During the flocculation period of 1.0 hour in these studies, pH values were generally observed to be in the range of 6.1 to 6.5, which was satisfactory for good floc formation and settleability of the floc. Results of these tests are summarized in Table 2. It can be seen from these data that the addition of calcium produced a slight increase in the amount of fluoride removed by alum flocculation. Data that show the effect of alum dosage upon the removal of fluoride in the coagulation process are presented in Table 3 and are graphically shown in Figure 1. Percentages of the initial fluoride concentration that were removed are plotted versus the alum dosages. The data show that fluoride removal with alum dosages up to 150 mg/l is approximately proportional to the amount of alum added, but above this level, the fluoride removal per unit

of alum added decreases. In Figure 2 the logarithm of the percent of the initial fluoride remaining after flocculation is plotted versus the alum dosage. The fluoride concentration is shown to decrease exponentially with increasing dosages of alum. The data for this plot was that obtained on the standard test waters for alum dosages of 50 to 300 mg/l. The initial fluoride concentrations of the test waters were 2.86 and 5.0 mg/l, respectively. The curves indicated that the removal of fluoride by alum coagulation was slightly more effective on the test water with the lower initial concentration of fluoride. The results of these tests compare favorably with the work of Culp and Stoltenberg (14). Comparative tests were made using sodium aluminate as the coagulant in one series and alum in the other, the aluminum concentration being the same for each test. These tests showed that alum was slightly more effective than an equivalent amount of sodium aluminate in fluoride removal.

Since the USEPA National Interim Primary Drinking Water Standards have indicated that the allowable level of fluoride should not exceed 1.4 to 2.4 mg/l, depending upon the maximum daily temperature, it would appear that the large dosages of alum necessary to meet this requirement would make this process for fluoride removal impractical for raw waters containing over 4.0 to 5.0 mg/l of fluoride. To obtain a fluoride residual of 2.0 mg/l for a water containing an initial fluoride concentration of 3.0 mg/l, one would require an alum dosage of approximately 75 mg/l. The alum dosage would be nearly 200 mg/l for a water having an initial fluoride content of 5.0 mg/l. Although these data indicate that the removal of fluoride is limited to waters that have a low initial fluoride content, the process is very effective in the removal of small amounts of fluoride from water.

Attempts to improve fluoride removal by alum flocculation were made using polyelectrolytes as coagulant aids in the process. Polyelectrolytes supplied by several manufacturers consisted of both strong and weak anionic and cationic polymers and non-ionics. All are potable flocculants that had received approval from the Environmental Protection Agency for treatment of drinking water at concentrations up to 1.0 mg/l.

At this stage in our study the necessary variables in the flocculation procedure had been determined and fluoride removal could be repeated for given coagulant dosages. Following this procedure, the effect of the various polyelectrolytes upon the removal of fluoride was determined. Initial tests indicated that additions of the polyelectrolytes immediately following the addition of alum increased the adsorption and removal of fluoride from 1.0 to 2.0 percent. Additional studies, however, indicated this increase was most likely due to improved flocculation and sedimentation rather than adsorption. Most of the coagulant aids formed larger and heavier flocs, but a few formed flocs of a much finer texture. In general, the anionics and non-ionics were more effective in our studies than were the cationics, but all of the coagulant aids shortened the sedimentation time and would be beneficial for alum coagulation.

In these studies the time periods for both flocculation and sedimentation were 0.5 hour. The shortened contact period did not appear to make any difference in the removal of fluoride. Immediate contact between the alum and the fluoride ions by rapid mixing and the stepwise addition of alum have been reported by other investigators to be important factors in the removal of fluoride by alum coagulation (14).

Table 1
The Effect of pH Upon Fluoride Removal from
Standard Test Water by Alum Coagulation

<u>Alum Dosage (mg/l)</u>	<u>pH</u>	<u>Calcium Added (mg/l)</u>	<u>Initial Fluoride (mg/l)</u>	<u>Residual Fluoride (mg/l)</u>	<u>Fluoride Removal (%)</u>
100	6.20	0	4.40	3.00	31.8
100	6.18	50	4.40	2.80	36.3
100	6.18	200	4.40	2.70	38.6
100	6.45	0	4.40	2.85	35.2
100	6.45	50	4.40	2.75	37.5
100	6.45	200	4.40	2.65	39.8
100	6.75	0	4.60	3.55	22.8
100	6.75	50	4.60	3.35	27.1
100	6.75	200	4.60	3.25	29.3

Table 2
 Fluoride Removal from Standard Test Water by Alum Coagulation,
 as Affected by the Addition of Calcium

Alum Dosage (mg/l)	pH	Calcium Added (mg/l)	Initial Fluoride (mg/l)	Residual Fluoride (mg/l)	Fluoride Removal (%)
50	6.20	0	5.00	3.92	21.0
50	6.20	50	5.00	3.80	24.0
50	6.20	100	5.00	3.80	24.0
100	6.42	0	5.00	3.25	35.0
100	6.40	50	5.00	3.15	37.0
100	6.41	200	5.00	3.05	39.0
100	6.48	0	5.00	3.22	35.0
100	6.45	50	5.00	3.15	37.0
100	6.41	200	5.00	3.05	39.0
150	6.25	0	4.70	2.55	45.7
150	6.25	50	4.70	2.45	47.8
150	6.30	200	4.70	2.35	50.0
200	6.34	0	4.70	2.09	56.3
200	6.30	50	4.70	1.95	58.5
200	6.27	200	4.70	1.92	58.9
250	6.20	0	4.75	1.55	67.3
250	6.20	50	4.75	1.65	65.2
250	6.18	200	4.75	1.45	69.4
300	6.20	0	4.75	1.30	72.6
300	6.18	50	4.75	1.25	73.6
300	6.10	200	4.75	1.20	74.7

Table 3
The Effect of Alum Dosage Upon Fluoride Removal from
Standard Test Water by Alum Coagulation

<u>Alum Dosage</u> (mg/l)	<u>pH</u>	<u>Calcium Added</u> (mg/l)	<u>Initial Fluoride</u> (mg/l)	<u>Residual Fluoride</u> (mg/l)	<u>Fluoride Removal</u> (%)
50	6.36	200	2.86	2.24	21.6
100	6.40	200	2.86	1.74	39.1
150	6.40	200	2.86	1.32	53.8
200	6.30	200	2.86	0.98	65.7
250	6.20	200	2.86	0.77	73.0
300	6.20	200	2.86	0.63	77.9

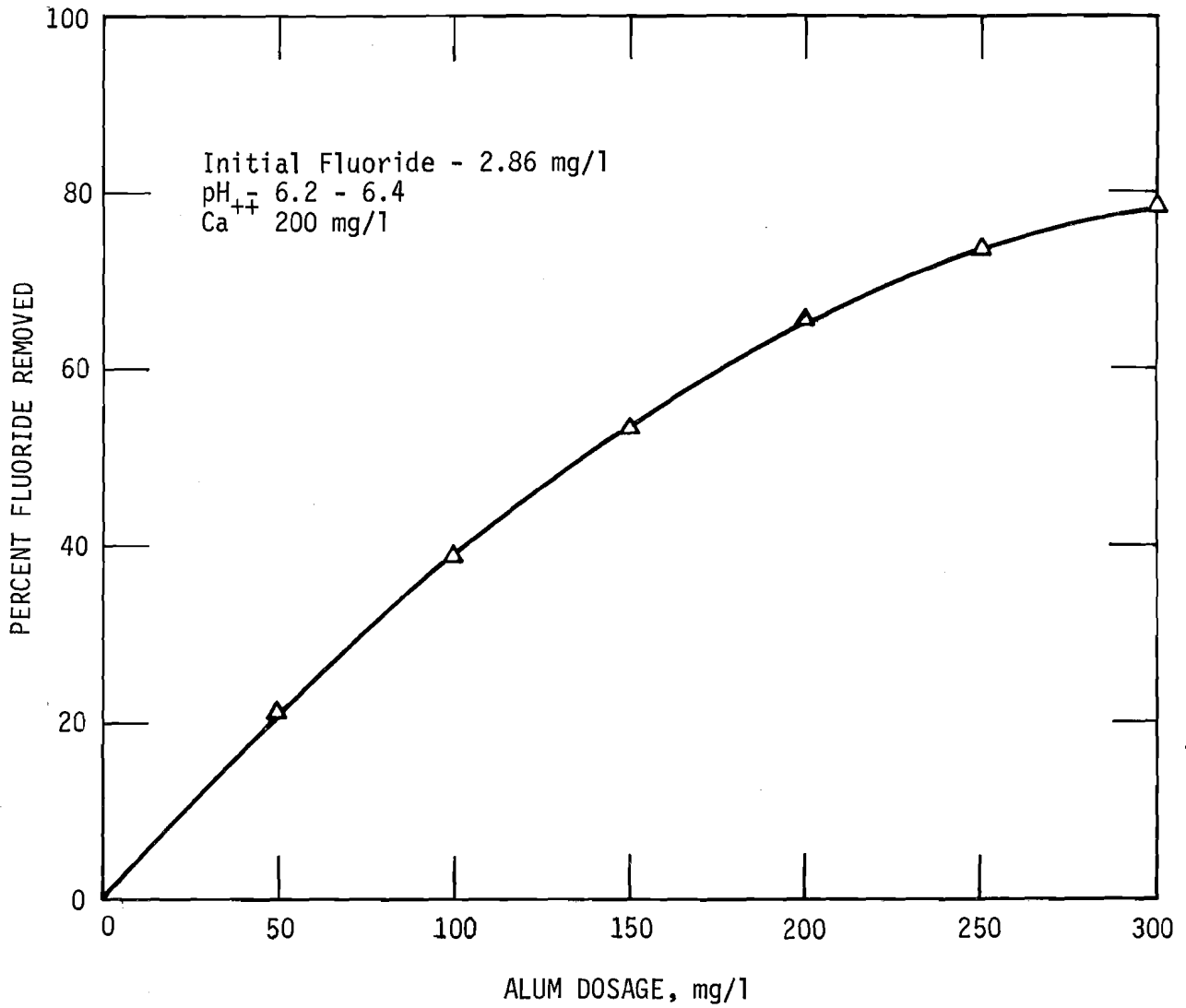


Figure 1. Effect of Alum Dosage Upon Fluoride Removal by Alum Coagulation

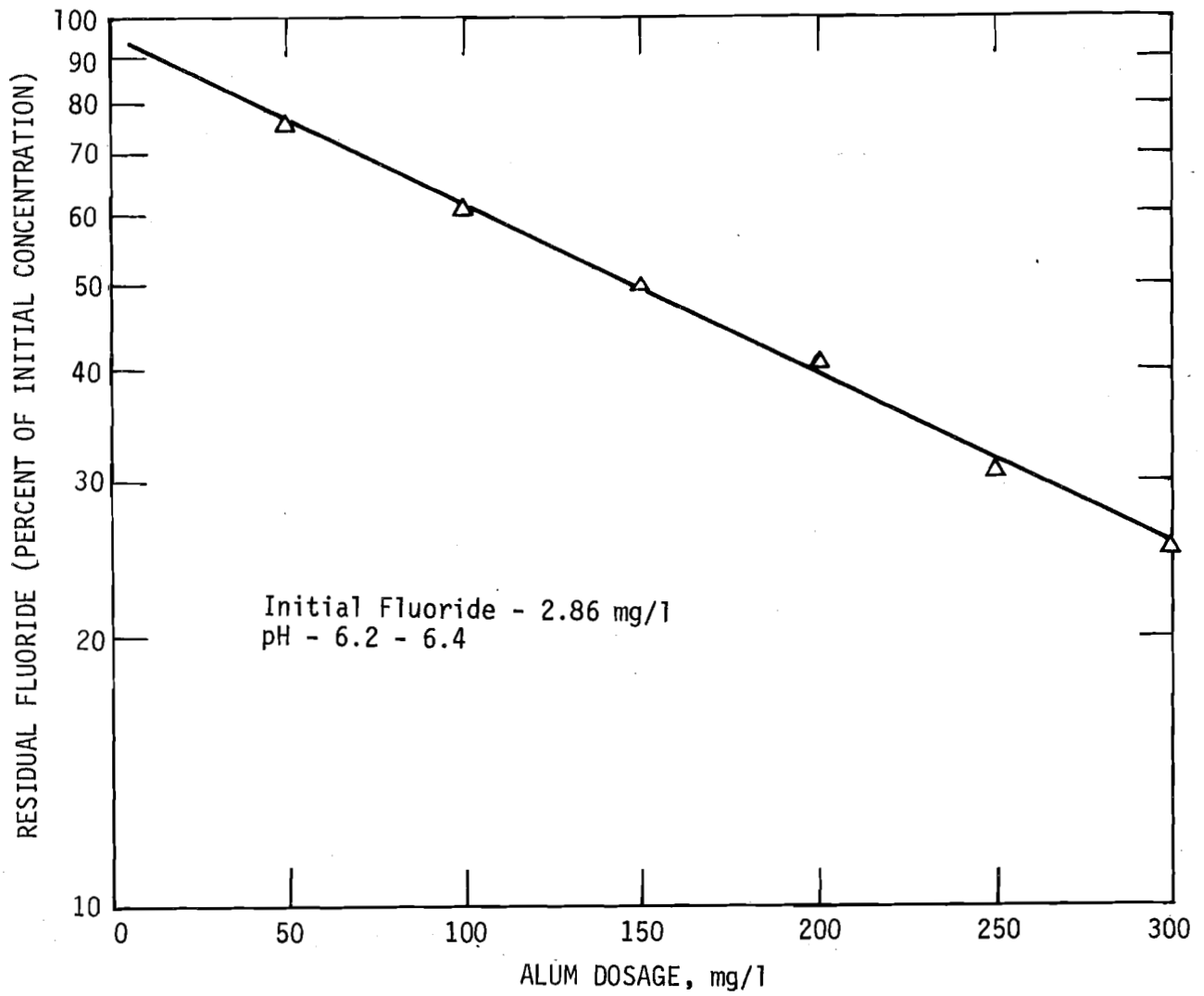


Figure 2. Residual Fluoride Expressed as the Percent of the Initial Fluoride Concentration Remaining after Alum Coagulation versus Alum Dosage

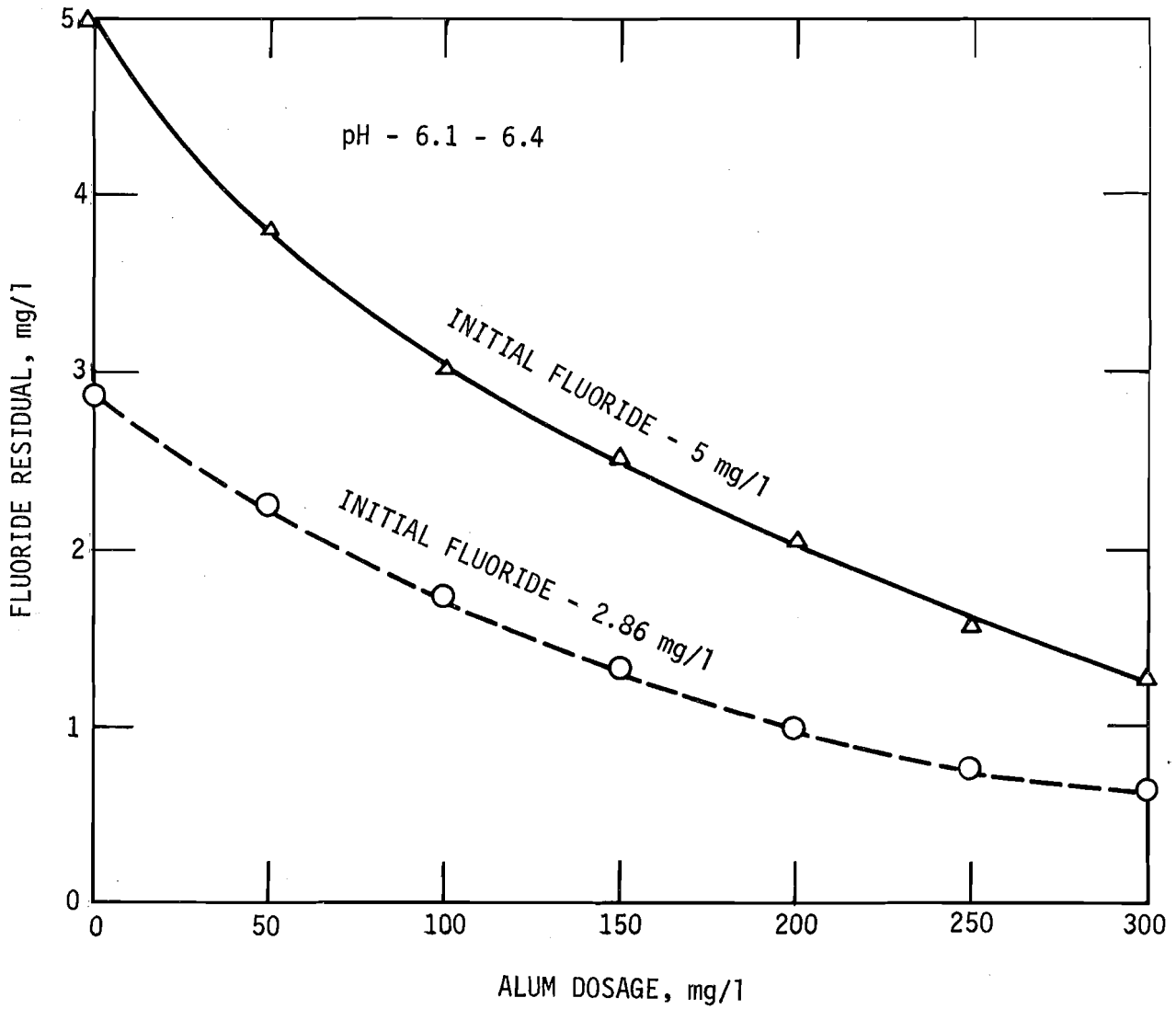


Figure 3. Fluoride Residuals Obtained after Alum Coagulation for Initial Fluoride Concentrations of 2.86 mg/l and 5.0 mg/l

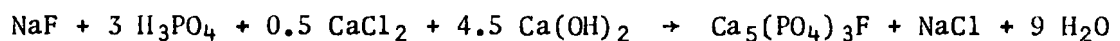
Fluorapatite Formation

One of the earliest methods proposed for the removal of fluoride from water was the use of degreased bone (17). The carbonate radical of the apatite in bone is replaced by anion exchange with fluoride, forming fluorapatite. Upon regeneration with caustic soda, the fluorapatite is converted to hydroxyapatite and the fluoride is removed as soluble sodium fluoride. Hydroxyapatite then becomes the exchange material formed, with the hydroxy radical replaced by fluoride. If the chemical reaction between phosphoric acid and lime is carefully controlled, tricalcium phosphate and hydroxyapatite are the products formed. This reaction with flocculation, sedimentation, and filtration can take place within the mixing basins of a conventional treatment plant (18).

The removal of fluoride from the standard test water by the addition of phosphate and calcium to form fluorapatite was investigated in a number of studies. Fluorapatite is a highly insoluble solid compound and its formation from hydroxyapatite has been reported as an effective means of fluoride removal (19). In several tests phosphoric acid was added to aliquots of the standard test water in concentrations that ranged from 50 to 315 mg/l. The results of several tests indicated that a minimum concentration of 190 mg/l (as PO_4) was required to remove approximately 50 percent of the fluoride from test waters that contained an initial fluoride concentration of 5.0 mg/l. In these tests calcium was added as calcium hydroxide to give a final pH of 9.5. At this pH level, the removal of phosphate was observed to be incomplete in some tests, and concentrations as high as 4.0 to 5.0 mg/l were observed. Further additions of calcium hydroxide to a pH level of 10.5 or more, however, reduced the phosphate residuals to amounts below 1.0 mg/l in most tests, and in

some tests values below 0.5 mg/l were observed. Fluoride reductions were also observed at the elevated pH levels due to the formation of magnesium hydroxide and subsequent adsorption of fluoride. In two tests where phosphate was added in amounts of 315 mg/l, the fluoride removals were observed to be 58.2 and 59.8 percent of the initial fluoride concentration, which was 4.95 mg/l.

In the previous tests described for the removal of fluoride by formation of fluorapatite, the calcium required for the reaction was added as calcium hydroxide. In a new process described for the removal of fluoride from drinking water or from industrial wastewater by Andco Environmental Processes, Inc. (20), the initial addition of calcium for the formation of fluorapatite is as calcium chloride. In this Andco system a solution of calcium chloride and phosphate is first added to the water stream containing fluoride, and the pH adjusted to 6.2 to 7.0 using a suspension of calcium hydroxide. With in-line mixing the water stream enters a holding tank for a 7-minute period, after which additional lime is added, with mixing, to a pH of 7.5 to 9.5. After the addition of a polyelectrolyte, the water stream enters a clarification tank, is settled and the final effluent water, which reportedly contains less than 0.5 mg/l of dissolved fluoride, is discharged. The fluorapatite sludge formed in the process is returned to the water stream at a point following the initial pH adjustment, or is disposed of in a waste stream. The chemical reaction represented by this process is represented as follows:



In several jar tests the removal of fluoride was determined by a procedure similar to the Andco process described. Using aliquots of the standard test water with varied amounts of fluoride added, the amount of

Table 4
 Percent of the Initial Fluoride Concentration Removed
 by Additions of Phosphoric Acid and Calcium Chloride

Phosphoric Acid (as PO ₄) mg/l	Initial Fluoride - mg/l					
	2.34	3.88	4.45	4.50	4.72	5.50
80	--	--	21.3	--	--	--
160	36.7	29.0	35.9	30.2	34.3	36.3
240	53.8	52.3	47.2	56.4	56.1	59.4
320	66.2	63.8	62.9	69.5	63.5	65.5
400	--	--	70.2	--	--	--

fluoride removed by the addition of several levels of phosphate and calcium was investigated. The results of several tests which show the percent of the initial fluoride that was removed by the various additions of phosphate and calcium are summarized in Table 4. Although some inconsistency in the data for the various tests was observed, the overall trend of the data indicated that the initial fluoride concentrations of the test waters had little effect upon the amount of fluoride removed by the various levels of phosphate added. The data obtained on the test water with an initial fluoride concentration of 4.45 mg/l were obtained by adding lime to a final pH of 10.0, bypassing the initial holding period at pH 6.2 to 7.0. With the exception of the low percentage of fluoride removed for the 240 mg/l phosphate dosage (47.2%), the remaining data agreed well with the other values reported. In this study the amount of calcium present in the phosphoric acid-calcium chloride solution was stoichiometric with relation to the amount of phosphate present in fluorapatite. Varied ratios of phosphate to calcium in this solution may have had some effect upon the removal of fluoride. The residual phosphate concentrations observed in these tests were generally less than 1.0 mg/l.

Removal with Magnesium

The removal of fluoride by lime softening of magnesium-containing waters was demonstrated by the early work of Boruff (11). Scott et al. (13) observed that the concentration of fluoride in municipal water supplies was substantially reduced by lime softening. In this process the fluoride is removed by adsorption on the precipitated magnesium hydroxide. The amount of fluoride removed is a function of the initial fluoride concentration and the amount of magnesium removed, as shown in the following equation:

$$F_r = F_i - (0.07 \times F_i \times \sqrt{Mg})$$

F_r and F_i represent the initial and final fluoride concentrations, and Mg represents the concentration of magnesium removed, all expressed in mg/l. Scott and his co-workers observed this relationship in both laboratory and full-scale operations. The laboratory tests were designed to produce a final fluoride concentration of 1.0 mg/l. Initial fluoride levels from 1.5 to 3.5 mg/l were used and the results were found to conform to the above relation between fluoride and magnesium removal.

The removal of fluoride by magnesium precipitation in lime softening cannot be considered as a generally applicable method of fluoride removal since it requires a fortuitous combination of fluoride and magnesium concentrations. Since such large quantities of chemicals are required, the process is useful only for low-fluoride-containing waters that require softening. If it were assumed that a water containing fluoride had a magnesium concentration of 40 mg/l, precipitation of the magnesium by lime treatment would reduce the fluoride concentration to a desired residual of 1.5 mg/l if the initial concentration of fluoride did not exceed 2.8 mg/l. To obtain a residual of 2.4 mg/l, the maximum concentration permitted by the USEPA, the initial concentration of fluoride could be as high as 4.1 mg/l. These values were determined from the equation previously defined. Some fluoride reductions are observed in water softening operations and this fluoride-magnesium relationship aids in explaining the observed losses. At several municipal water plants in the U.S. where fluoride is present in the raw water in concentrations of 2.0 to 3.0 mg/l, fluoride is removed along with the magnesium hardness by this process (7).

Table 5
 Fluoride Removal in Relation to Magnesium Removal from
 Standard Test Water that Contains Initial Concentrations
 of Magnesium of 49, 73, and 24 mg/l

<u>pH</u>	<u>Magnesium - mg/l</u>			<u>Fluoride - mg/l</u>		
	<u>Initial</u>	<u>Residual</u>	<u>Removed</u>	<u>Initial</u>	<u>Residual</u>	<u>Removed</u>
11.00	0	0	0	4.30	4.15	0.15
10.83	49	6	43	4.30	2.30	2.00
10.84	73	7	66	4.30	1.85	2.45
10.92	24	11	13	2.35	1.90	0.45

Initial studies in our laboratory on fluoride removal by magnesium flocculation showed that calcium was necessary for the formation of a satisfactory floc in the coagulation process. Floccs formed using our standard test water that had a hardness of 200 mg/l (as CaCO_3) and due entirely to the magnesium added were soft and fluffy in appearance and settled with difficulty. Fluoride removal was approximately 28 percent of the initial concentration in these studies. The addition of calcium in similar tests improved the texture and settleability of the floccs, but the percentages of fluoride removed were essentially the same. The effect of polyelectrolytes as coagulant aids was studied in a few tests. Anionic polyelectrolytes were shown to increase the particle size and settling rate of the floccs formed but the non-ionics tested had no visible effect upon the process. In these tests sodium hydroxide was used to adjust the pH to values between 10.7 and 11.0.

The effect of magnesium upon fluoride removal by the lime-soda process was studied by the usual jar test procedure. Our standard test water was modified in these tests with the initial concentrations of magnesium added in amounts of 24, 49, and 73 mg/l (as Mg^{++}). The initial fluoride concentrations were 4.30 and 2.35 mg/l. The initial pH of these solutions was 8.19 but ranged from 10.8 to 10.9 upon the addition of calcium hydroxide and sodium bicarbonate. The slow addition of the lime slurry during the rapid mix period of the procedure required approximately 5 minutes of the 30-minute flocculation period. Floc formation in these tests was satisfactory and was quite rapid, so the addition of a flocculant aid was not necessary. The results of these tests showing the relationship of magnesium and fluoride removal are summarized in Table 5. From these data it can be seen that the removal of fluoride is proportional

to the amount of magnesium removed in the formation of the magnesium hydroxide floc. Tests with initial magnesium concentrations of 49 and 73 mg/l produced magnesium removals of 43 and 66 mg/l from the respective solutions. These removals represent 87.7 and 90.4 percent of the initial magnesium concentrations. The removal of fluoride in these solutions is directly related to the respective magnesium removals expressed by the equation of Scott (13). The observed fluoride residuals of 2.30 and 1.85 mg/l compared favorably with the calculated fluoride residuals of 2.31 and 1.86 mg/l. The removal of fluoride from the test water that contained lower initial concentrations of fluoride and magnesium (2.35 and 24.0 mg/l, respectively) was not exactly in agreement with the equation. The calculated residual was 1.76 mg/l as compared with the observed value of 1.90 mg/l. This is considered to be in reasonable agreement considering experimental error.

Iron Salts as Coagulants

Limited data are available on the use of iron salts as coagulants for the removal of fluoride from drinking water, but a few reports have described their use for the removal of fluoride from wastewaters (6,21,22). A series of tests were undertaken in our laboratory to determine if such factors as pH and the concentration of the coagulant would have a beneficial effect upon fluoride removal. Various amounts of ferric sulfate were added to 1-liter aliquots of the standard test water that contained 5.0 mg/l of fluoride and had the pH adjusted to values within the range of 4.1 to 9.7. The concentration of ferric sulfate used in these tests ranged from 22 to 175 mg/l (as Fe^{+++}). The results of these tests showed that excellent flocs were formed that settled rapidly, but these flocs were very ineffective in the removal of fluoride. Analyses made on the

clarified solutions indicated that less than 5.0 percent of the initial fluoride concentration was removed from the solutions with a pH above 6.0. A few tests at pH levels below 6.0 produced somewhat increased fluoride removals, but the fraction of fluoride removed was still too low to be of interest. Similar studies using ferric chloride also showed fluoride removals of less than 5.0 percent of the initial fluoride present. Tests in which the standard test water was first treated with lime, precipitated at pH 12.0, and filtered prior to coagulation with either ferric or ferrous sulfate, resulted in fluoride removals, due to the iron flocculant, of 2.6 to 10.5 percent of the initial fluoride. The removal of fluoride that resulted from the lime treatment prior to flocculation was approximately 25 to 30 percent of the initial fluoride. This removal was due to the adsorption of fluoride on the magnesium hydroxide formed from the magnesium content of the test water. In general, the results of this series of tests indicate that some fluoride can be removed by flocculation with iron salts, but the amount removed is not significant.

Removal with Charcoal

The removal of fluoride from water by powdered activated charcoal has been reported to be a pH dependent process that requires a pH of 3.0 or less for the adsorption of fluoride (23). Although this low pH would make its use impractical from a standpoint of water treatment, a few tests were made to determine its effect upon fluoride removal. Tap water supplemented with fluoride and adjusted to pH values that ranged from 5.5 to 7.0 was passed through columns packed with activated charcoal. Analyses of the effluents showed that no fluoride had been adsorbed.

In a series of jar tests the removal of fluoride from aliquots of the standard test water by activated charcoal was determined. The pH of

these solutions had been adjusted to 3.0, 5.0, and 7.0. The results of these tests showed that no adsorption of fluoride occurred in the solutions adjusted to pH 5.0 and 7.0, but in the solution adjusted to pH 3.0, approximately 16.0 percent of the initial fluoride was removed. This effect of pH upon fluoride removal by activated carbon is explainable upon the basis of dissociation of the hydrofluoric acid molecule. Only the undissociated molecule can be adsorbed, and at higher pH values, most of the fluoride exists as the ion rather than as the acid.

Studies with animal (bone black) charcoal, on the other hand, indicated its possible use for the removal of fluoride from water. Animal charcoal or bone char is essentially tricalcium phosphate and carbon. The ground animal bones have been charred to remove all organics. This material has been effectively used as an adsorbent in the removal of fluoride. In jar tests with fluoride-supplemented tap water, the addition of animal charcoal with alum as the coagulant was found to produce fluoride removals proportional to the additions of animal charcoal. The alum dosage in these tests was 200 mg/l. Animal charcoal added in amounts of 100, 200, and 300 mg/l resulted in fluoride removals of 4.1, 8.9, and 13.8 percent of the respective initial concentrations over the amount removed by the alum alone. The removal of fluoride appeared to be slightly more effective at pH 7.2 than at 6.7. In similar tests several polyelectrolytes were added along with the animal charcoal to assist in the formation of the alum floc. The flocculant aids were added in concentrations of 1.0 mg/l and the amount of animal charcoal added was 200 mg/l. The alum dosage was 200 mg/l as in the previous test. In these tests the standard test water used was adjusted to pH values that ranged from 6.4 to 7.0. The initial fluoride concentration was 4.5 mg/l. Upon floccu-

lation, the alum removed 53.0 percent of the initial fluoride, but this removal was increased an additional 9.0 percent in the tests with the added charcoal. In tests with the polyelectrolyte additions, the flocs formed were more desirable, but the amount of fluoride adsorbed was not increased significantly.

In view of these results it was of interest to compare the effect that animal charcoal would have upon the removal of fluoride by sodium aluminate. The amount of alum added in these tests was 200 mg/l, and the amount of sodium aluminate added contained aluminum in an amount comparable to the amount in the alum addition. The results of these tests indicated that fluoride removal by alum was slightly more effective than by aluminate flocculation. In tests with the animal charcoal added prior to flocculation, fluoride removal was increased approximately 8.0 to 9.0 percent for both alum and aluminate. The addition of polyelectrolytes as coagulant aids showed a negligible increase in the removal of fluoride.

Although the addition of animal charcoal to a water supply for the removal of fluoride without the addition of a primary flocculant would be unlikely, the extent of fluoride removal by the addition of animal charcoal alone was of interest. Aliquots of the standard test water that were adjusted to pH 6.5, and had fluoride added in concentrations of 1.98, 4.16, 4.95, and 7.50 mg/l, were treated with animal charcoal for the removal of fluoride in jar tests. The concentration of animal charcoal added to the solutions was 200 mg/l. The results of these tests showed a range of fluoride removals of 12.0 to 16.6 percent of the initial fluoride concentrations for the respective solutions. The mixing and settling time periods in these tests were extended over those of

the previous tests with alum, which may account, in part, for the increased fluoride removals. The addition of animal charcoal to aliquots of the standard test water that had been treated for the removal of fluoride by the lime-soda softening process, increased the removal of fluoride 5.3 and 6.6 percent in separate tests. Precipitation of the test water at pH 10.8 with 240 mg/l of calcium hydroxide removed 26.9 percent of the initial fluoride concentration. Animal charcoal (300 mg/l) added to similarly treated aliquots, removed 33.5 and 32.2 percent of the fluoride in the respective tests.

Treatment with Alum and Phosphoric Acid

The removal of fluoride from wastewater by a combined alum-phosphoric acid treatment was proposed by Nishimura, et al. (24). In this method, alum was added first, followed by phosphoric acid, calcium chloride, sodium hydroxide, and finally, lime. Both an aluminum complex and fluorapatite were considered to be formed and removed in a single flocculation-sedimentation step.

In a few tests using the standard test water, fluoride removal by this one-step procedure was compared with the amount of fluoride removed by the individual treatments of alum coagulation and fluorapatite formation, and by the combination treatment in which the test water was filtered after alum coagulation and before fluorapatite formation. The results of these studies indicated that the fluoride removal by the combined treatment was less than that obtained when the alum flocculation and fluorapatite precipitation were applied separately. These results were predictable, due to the amphoteric nature of the aluminum hydroxide and its reentrance into solution at the higher pH. In the combined

treatment where the alum floc was removed by filtration prior to the formation of fluorapatite, the fluoride removal was equal to that obtained by sequential application of the individual treatments.

In these tests the percent of the initial fluoride concentration removed by alum dosages of 100 and 200 mg/l were in agreement with the values shown in Figure 1. The percent removals for the phosphate additions of 160 mg/l were also in agreement with values observed in previous tests (Table 4).

Removal with Coagulant Aids

Several of the coagulant aids that were made available for this study were also reported to be useful as primary coagulants to replace alum or iron salts in the treatment of municipal and industrial water supplies. Since the colloidal particles in natural water supplies usually carry a negative charge, cationic polyelectrolytes were the logical choice to be studied as possible agents for fluoride removal. When used as primary coagulants in water treatment, the use of a specially selected clay is recommended by the manufacturer of one such coagulant. The clay is helpful when mixing time is short. In jar tests, bentonite was added to aliquots of the standard test water in concentrations that ranged from 2.0 to 10.0 mg/l. The concentration of the polyelectrolytes added was limited to 1.0 mg/l or 5.0 mg/l in order to be within the limits approved by the EPA for the polyelectrolyte in question. The flocs formed in these tests were slow to build, but within an hour of stirring time at 20 rpm, they became quite dense and settled well. Fluoride removals observed in the clarified solutions, however, were not significant since only 1.8 to 4.4 percent of the initial fluoride concentration was removed.

alkalinity adsorption by the column.

It is quite apparent from the results of these basic tests that the alkalinity of the influent water is quite competitive with the fluoride exchange capacity of the alumina. This process has been studied in considerable detail in the laboratory and has been applied in large-scale operations.

SUMMARY

A variety of methods for the removal of fluoride from potable water were tested in this study with emphasis placed upon coagulation methods.

Coagulation with alum at pH levels of 6.2 to 6.4 was one of the more effective methods tested. With a test water containing 5.0 mg/l of fluoride, application of 200 mg/l of alum produced a 60% reduction in the fluoride content.

Fluoride can also be removed by a process which is based upon the formation of fluorapatite. With 4.72 mg/l of fluoride in the test water, this concentration was reduced 63% by the application of 320 mg/l of phosphate, with the appropriate calcium addition and pH control.

Fluoride is also removed by adsorption on magnesium hydroxide. This occurs to some extent in many softening processes. In a test water with 4.30 mg/l of fluoride and 73 mg/l of magnesium ion, treatment with lime to precipitate 90% of this magnesium also reduced the fluoride concentration by 57%.

Flocculation with iron salts following calcium precipitation has been reported to be effective with wastewaters, but our tests showed little or no benefit from this treatment. Ferric chloride and sulfate, as well as ferrous sulfate, were included in these tests. With 5.0 mg/l of fluoride and up to 175 mg/l of ferric sulfate or chloride (as Fe) the fluoride removed was from 2 to 10% of the initial concentration.

Several other methods, such as the use of activated carbon, were tested but without any appreciable success. Flocculant aids were found helpful in obtaining good clarification for some processes, and thereby aided in fluoride removal.

For comparative purposes, some work was done with an activated alumina column. This method is quite effective in removing fluoride. The disadvantage is that the activated alumina removes both alkalinity and fluoride ion. Thus the capacity of an activated alumina column for fluoride removal and the quantity of chemicals for regeneration are dependent upon both the fluoride content and the alkalinity of the untreated water. This process has been studied in great detail by others. Emphasis, in this study, was placed on the other methods involving chemical treatment, flocculation, and sedimentation.

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REFERENCES

- 1 Prival, M. J., and Fisher, F., "Adding Fluorides to the Diet,"
Environment 16, 29-33 (1974).
- 2 Hodge, H. C., and Smith, F. A., "Some Public Health Aspects of Water
Fluoridation, Fluoridation as a Public Measure," A.A.A.S.
(J. H. Shaw, editor). Publ. No. 38, Washington, D. C. (1954).
- 3 Roholm, K., "Fluoride Intoxication. A Clinical-Hygiene Study,"
H. K. Lewis & Co., Ltd., London (1937).
- 4 Watson, I. C., Spano, S. J., Davis, H. N., and Heider, F. M.,
"Monograph of the Effectiveness and Cost of Water Treatment
Processes for the Removal of Specific Contaminants,"
Volume 1, Technical Manual Prepared for Environmental
Protection Agency, (August 1974).
- 5 Sorg, Thomas J., "Treatment Technology to Meet the Interim Primary
Drinking Water Regulations for Inorganics," Jour. AWWA 70,
105-112 (1978).
- 6 Link, W. E., and Rabosky, J. G., "Fluoride Ion Removal from
Wastewater Employing Calcium Precipitation and Iron Salt
Coagulation," 31st Purdue Industrial Waste Conference,
May 7-9, 1974 (Lafayette: Purdue University Press, 1974).
- 7 Savinelli, E. A., and Black, A. P., "Defluoridation of Water with
Activated Alumina," Jour. AWWA 50, 33-43 (1958).
- 8 Maier, F. J., "Defluoridation of Municipal Water Supplies,"
Jour. AWWA 45, 879-888 (1953).
- 9 Bellack, E., "Arsenic Removal from Potable Water," Jour. AWWA 63,
454-458 (1971).
- 10 "Standard Methods for the Examination of Water and Wastewater,"
(14th edition), American Public Health Association, Inc.,
New York (1975).
- 11 Boruff, C. S., "Removal of Fluorides from Drinking Waters,"
Ind. Eng. Chem., 26, 69-71 (1934).
- 12 Kempf, C. A., Greenwood, D. A., and Nelson, V. E., "The Removal of
Fluoride from Drinking Waters in the State of Iowa,"
J. Iowa Acad. Sci., 41, 153 (1934).
- 13 Scott, R. D., Kimberly, A. E., Van Horn, A. L., Ey, L. F., and
Waring, F. H., "Fluoride in Ohio Water Supplies-Its Effect,
Occurrence, and Reduction," Jour AWWA 29, 9-25 (1937).

- 14 Culp, R. L., and Stoltenberg, H. A., "Fluoride Reduction at LaCrosse, Kansas," Jour. AWWA 50, 423-431 (1958).
- 15 Zabban, W., and Helwick, R., "Defluoridation of Wastewater," 30th Purdue Industrial Waste Conference, May 6-8, 1975 (Lafayette: Purdue University Press, 1975).
- 16 Rabosky, J. G, and Miller, J. P., Jr., "Fluoride Removal by Lime Precipitation and Alum and Polyelectrolyte Coagulation," 29th Purdue Industrial Waste Conference, May 7-9, 1974 (Lafayette: Purdue University Press, 1974).
- 17 Smith, H. V., and Smith, M. C., "Bone Contact Removes Fluorine." Wtr. Works Eng., 90, 600 (1937).
- 18 MacIntire, W. H., and Hammond, J. W., "Removal of Fluorides from Natural Waters by Calcium Phosphate," Ind. Eng. Chem., 30, 160-162 (1938).
- 19 Adler, H., Klein, G., and Lindsay, F. K., "Removal of Fluorides from Potable Water by Tricalcium Phosphate," Ind. Eng. Chem., 30, 163-165 (1938).
- 20 Andco Environmental Processes, Inc., 2005 Walden Ave., P.O. Box 988, Buffalo, New York.
- 21 Japanese Patent No. 7507,353, "Removal of Fluoride from Waste Water," assigned to M. Wakui, Y. Tobeta, M. Aizawa (Hitachi, Ltd.) (January 25, 1975).
- 22 Japanese Patent No. 7515,356, "Removal of Fluoride from Waste Water," assigned to Y. Yokota, S. Yoshikawa, S. Ikeda, Y. Fujimoto, and M. Hayano (Dai Nippon Toryo Co., Ltd.) (February 18, 1975).
- 23 McKee, R. H., and Johnston, W. S., "Removal of Fluorides from Drinking Water," Ind. Engrg. Chem., 26, 849 (1934).
- 24 Japanese Patent No. 7699,853, "Treatment of Fluorine Containing Waste Water," assigned to S. Nishimura, T. Sawa, K. Ohtani, S. Kitsukawa (Hitachi, Ltd.) (September 3, 1976).
- 25 Bishop, Paul L., "Fluoride Removal from Drinking Water by Fluidized Activated Alumina Adsorption," Proceedings AWWA 96th Annual Conference, Volume 2, Water Technology and Research, New Orleans, La., 1-15, June 20-25, 1976.