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Fluoride Removal from Potable Water Supplies

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FINAL REPORT

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ABSTRACT

FLUORIDE REMOVAL FROM POTABLE WATER SUPPLIES

The objective of this project was to determine whether or not the fluoride level in waters with moderate fluoride content (2 to 10 mg/1) could be reduced to acceptable levels by chemical treatment. The optimum concentration for dental health is from 1.1 to 1.8 mg/1. 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/1 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/1 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/1. 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/1 with approximately 50% of these levels in excess of 2.2 mg/1. In addition, there are a number of scattered sites throughout the state that have fluoride levels in excess of 8 ng/1. 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 method' have been presented by Sorg (5), Link and Rabosky (6), Savinelli and Black (7), and Maier (8). A technical manual which compares the effectivenes ; 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 rag/1. 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:

	mg/1	
$NaHCO_3$	168.0	
$CaCl_2 \cdot 2H_2O$	40.0	(as Ca++)
$MgCl_2 \cdot 6H_2O$	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:

	mg/1		mg/1
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 1x3 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/1. 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 mis 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/1 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/1 by an alum dosage of 200 mg/1. 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/1. 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/1 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/1. The initial fluoride concentrations of the test waters were 2.86 and 5.0 mg/1, 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/1, 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/1 of fluoride. To obtain a fluoride residual of 2.0 mg/1 for a water containing an initial fluoride concentration of 3.0 mg/1, one would require an alum dosage of approximately 75 mg/1. The alum dosage would be nearly 200 mg/1 for a water having an initial fluoride content of 5.0 mg/1. 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/1.

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

Alum Dosage (mg/1)	pH	Calcium Added (mg/1)	Initial Fluoride (mg/1)	Residual Fluoride (mg/1)	Fluoride Removal (%)
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/1)	pH	Calcium Added (mg/1)	Initial Fluoride (mg/1)	Residual Fluoride (mg/1)	Fluoride Removal (%)
SO	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

Alum Dosage (mg/1)	pH	Calcium Added (mg/1)	Initial Fluoride (mg/1)	Residual Fluoride (mg/1)	Fluoride Removal (%)
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

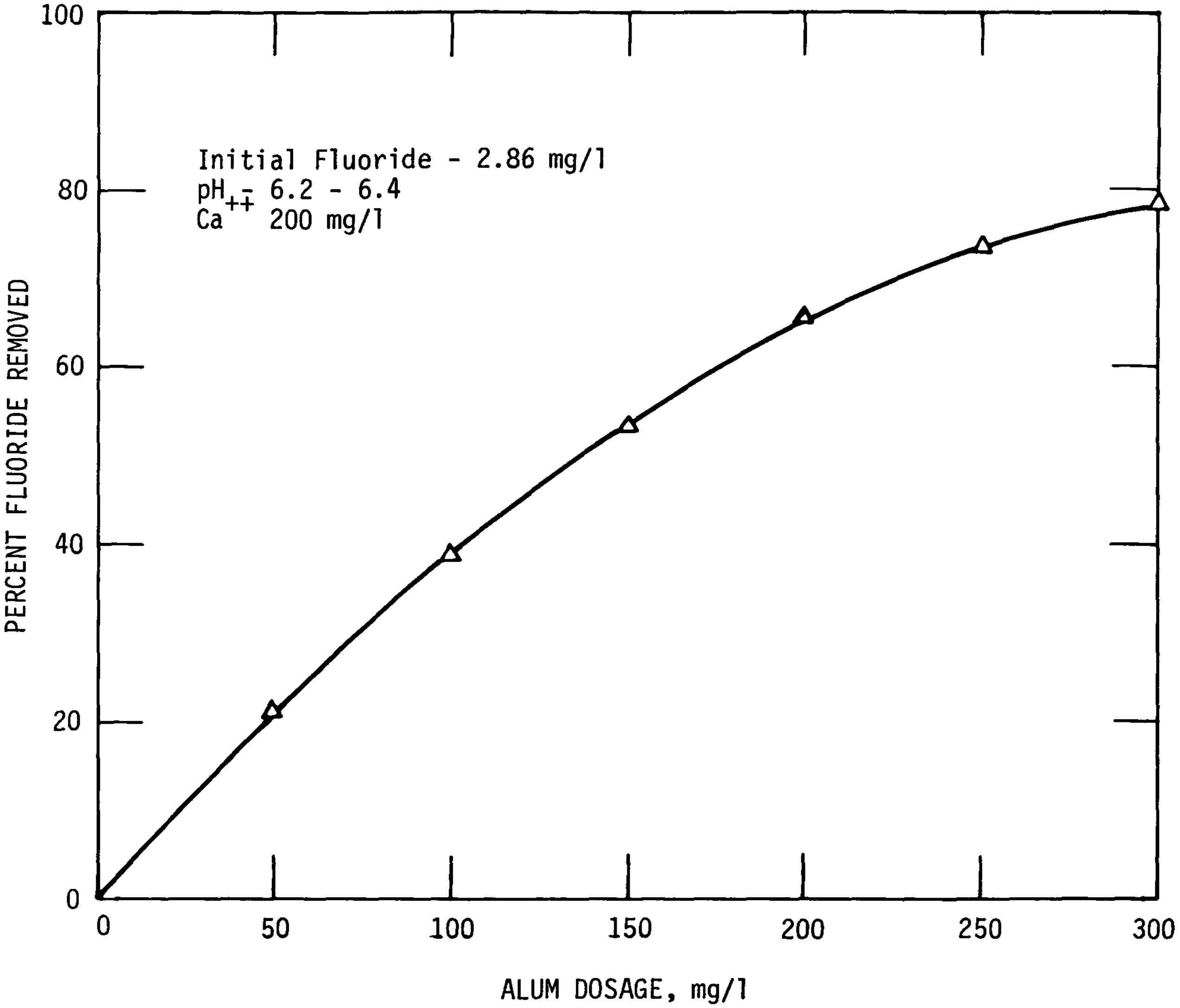

Figure 1. Effect of Alum Dosage Upon Fluoride Removal by Alum Coagulation

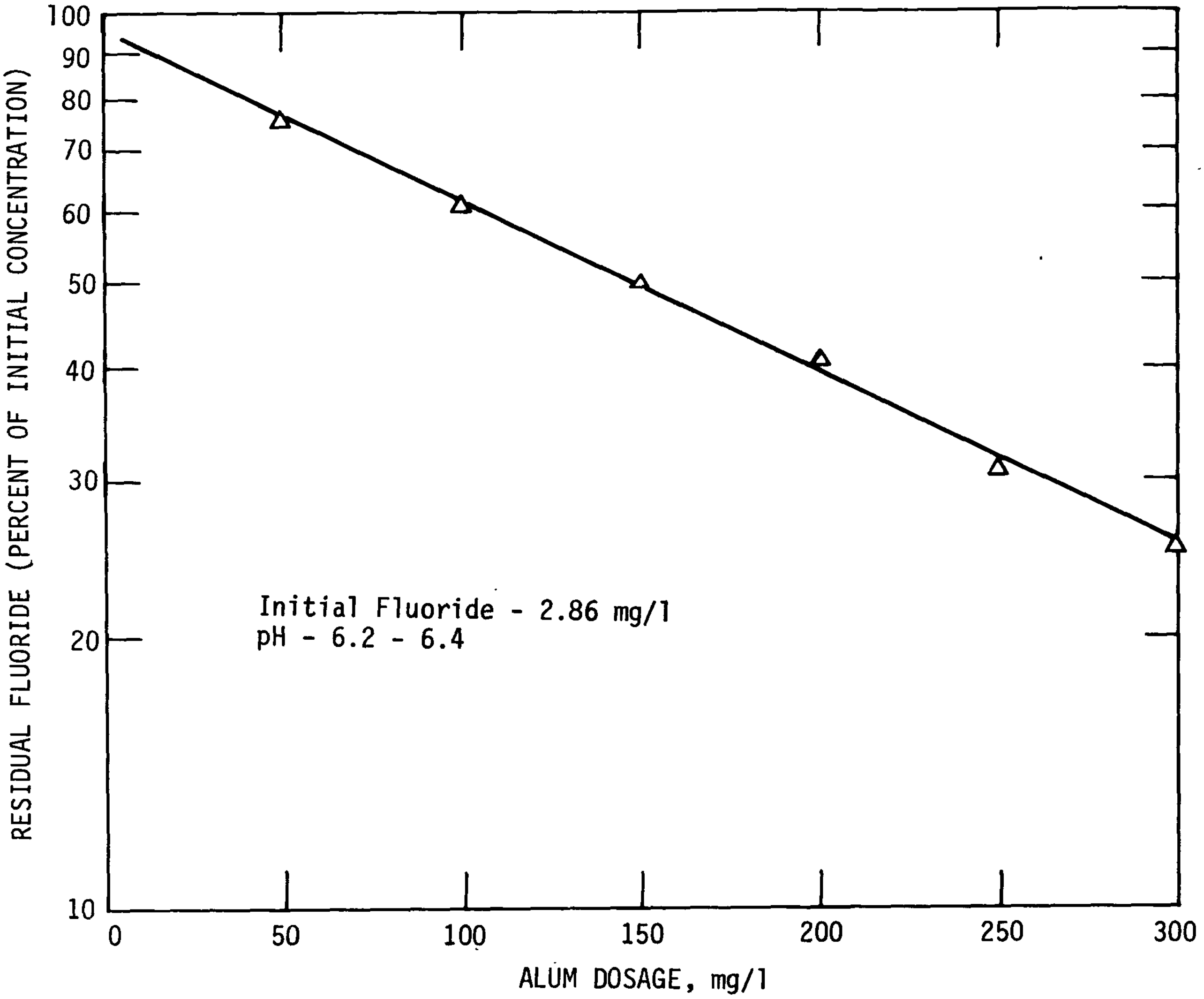

Figure 2. Residual Fluoride Expressed as the Percent of the Initial Fluoride Concentration Remaining after Alum Coagulation versus Alum Dosage

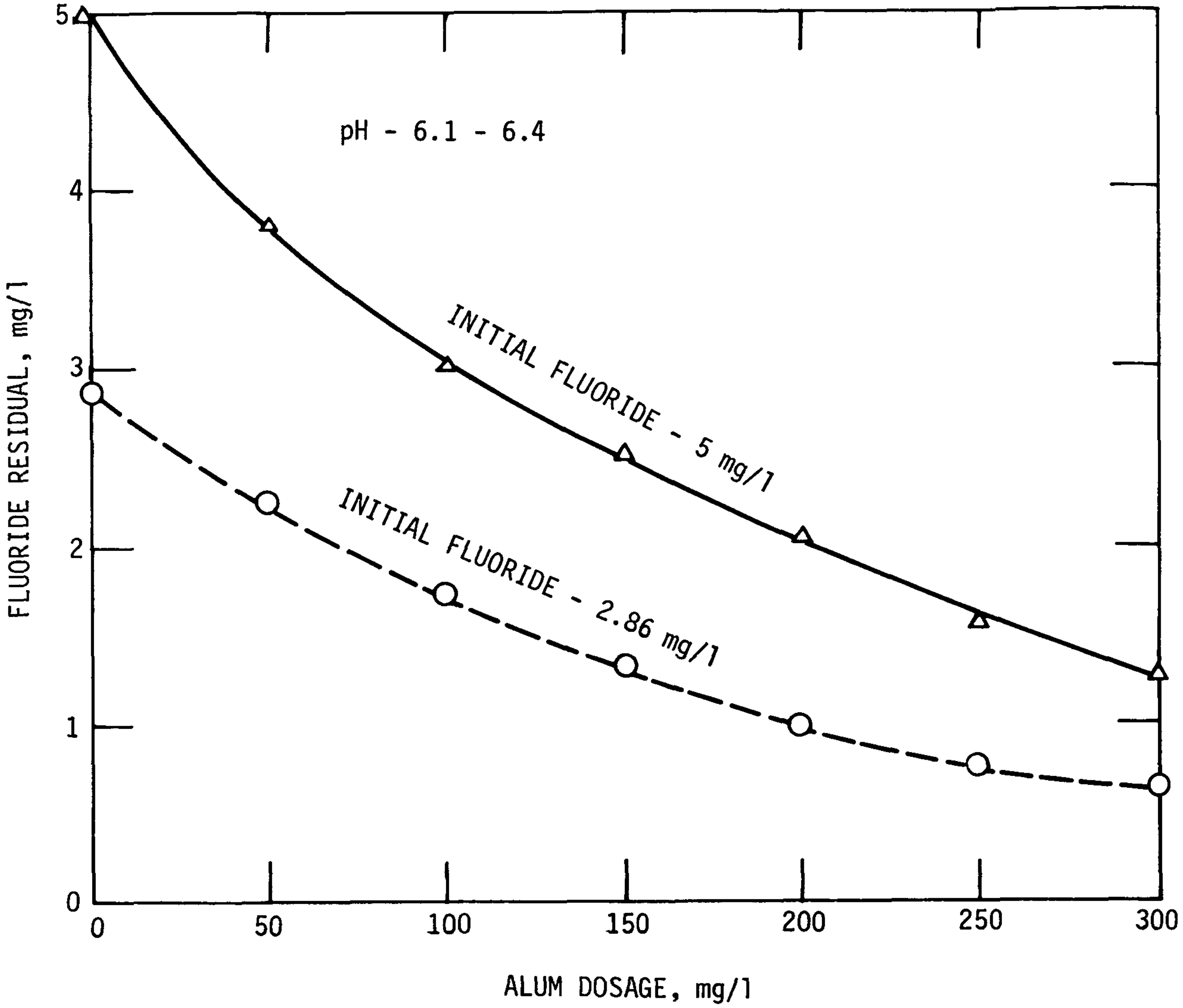

Figure 3. Fluoride Residuals Obtained after Alum Coagulation for Initial Fluoride Concentrations of 2.86 mg/1 and 5.0 mg/1

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 rag/1. The results of several tests indicated that a minimum concentration of 190 mg/1 (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/1. 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/1 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/1 in most tests, and in some tests values below 0.5 mg/1 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 rag/1, the fluoride removals were observed to be 58.2 and 59.8 percent of the initial fluoride concentration, which was 4.95 mg/1.

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/1 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:

$$NaF + 3\ H_3PO_4 + 0.5\ CaCl_2 + 4.5\ Ca(OH)_2 \rightarrow Ca_5(PO_4)_3F + NaCl + 9\ H_2O$$

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	Initial Fluoride - mg/1					
(as PO_4) mg/1	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	--	--	--