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Chapter 20 Fluoridation and Defluoridation

INTRODUCTION

The element fluorine is found in every water supply used for drinking purposes.¹ Fluorine is required for the formation of bones and teeth, and fluoride ions are essential to the normal growth and development of humans.

This chapter reviews the history of research on fluorides in drinking water, followed by a description of the chemicals used for fluoridation and the techniques used for fluoride addition to drinking water. Also, methods are described for the removal of fluorides in situations where their concentration is too great to allow potable use of the water supply.

FLUORIDE RESEARCH

During the past century, U.S. immigration officials noticed that people arriving from certain parts of Europe were severely afflicted by a disfigurement of the teeth known as mottled enamel or dental fluorosis. This led dental authorities to believe that the disfigurement was due to a local factor endemic to the immigrants' native land. Soon after, reports began to appear of mottled enamel among people native to the United States. These reports came largely from cities in the Great Plains and Rocky Mountain states.

Substantial evidence that fluorides were the cause of mottled enamel was obtained by H. V. Churchill in 1930.² The people of Bauxite, Arkansas reported a high incidence of mottled enamel. Churchill, by spectrographic analysis, found appreciable amounts of fluoride ion in the Bauxite water supply. In collaboration with F. S. McKay, a dentist, he studied waters from five areas where mottling was endemic and 40 areas where it was not a problem. From these studies, it was concluded that excessive fluoride levels in the drinking water caused the mottled enamel.³ Further proof was reported by Smith et al., who found that mottled enamel could be produced in white rats by adding to their diets either small amounts of fluoride salts or the concentrated residues from waters known to cause mottled teeth in humans.⁴

Finally, Gottlieb in 1934 reported on the relationship between fluoride concentration and mottling.⁵ She found that in Kansas communities reporting mottled enamel, the concentrations of fluoride in the municipal drinking water supplies were in excess of 2 mg/l.

In 1938, Dean presented data demonstrating that dental caries were less prevalent when mottled enamel occurred.⁶ This led to extensive correlation studies on dental caries versus fluoride levels in drinking waters throughout the United States. The results obtained, as summarized by Dean, are presented in Fig. 20-1.⁷ From this information, and the dental fluorosis data, a dental caries-fluoride relationship evolved:

1. When the fluoride level exceeds about 1.5 mg/l, any further increase does not significantly decrease the incidence of decayed, missing, or filled teeth, but does increase the occurrence and severity of mottling.
2. At a fluoride level of approximately 1.0 mg/l, the optimum effect occurs, that is, maximum reduction in caries with no aesthetically significant mottling.
3. At fluoride levels below 1.0 mg/l, some benefit occurs, but dental caries reduction is not great, and it gradually decreases as the fluoride levels decrease until, as zero fluoride is approached, no observable improvement occurs.

From the relationship between dental caries and fluoride concentration, the allowable and recommended fluoride concentrations shown in Table 20-1 were determined. The recommended fluoride concentrations decrease with

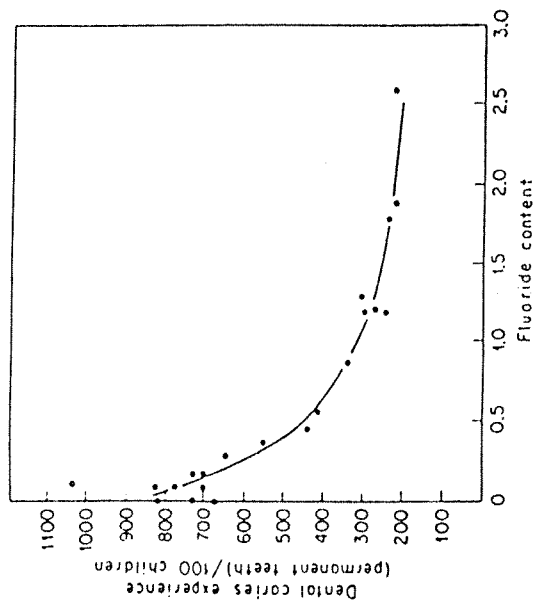


Fig. 20-1. Relationship between dental caries and fluoride level in drinking water.⁷

Table 20-1. Recommended and Approved (Health) Limits for Fluoride in Drinking Water.

ANNUAL AVERAGE OF MAXIMUM DAILY AIR TEMPERATURES, °F (°C) BASED ON TEMPERATURE DATA OBTAINED FOR A MINIMUM OF 5 YEARS	RECOMMENDED LIMITS, mg/l			APPROVED, mg/l
	LOWER	OPTIMUM	UPPER	
50.0 to 53.7 (10 to 12.1)	0.9	1.2	1.7	1.8
53.8 to 58.3 (12.1 to 14.6)	0.8	1.1	1.5	1.7
58.4 to 63.8 (14.6 to 17.7)	0.8	1.0	1.3	1.5
63.9 to 70.6 (17.7 to 21.4)	0.7	0.9	1.2	1.4
70.7 to 79.2 (21.5 to 26.2)	0.7	0.8	1.0	1.2
79.3 to 90.5 (26.3 to 32.5)	0.6	0.7	0.8	1.1

* Reference 8.

increasing temperature because more water is consumed during warm weather periods than at cooler temperatures.

It was noted earlier that all water supplies contain fluoride. Therefore, it can be said that all water supplies are fluoridated. However, because waters with fluoride concentrations of less than 0.7 mg/l do not have appreciable dental significance, they are generally referred to as "naturally fluoridated." For drinking water with fluoride concentrations below 0.7 mg/l, "controlled fluoridation" is used to increase the concentrations.

The effectiveness of controlled fluoridation has been tested in 10-year studies in such cities as Newburgh, New York and Grand Rapids, Michigan. The investigations demonstrated the safety of controlled fluoridation and its effectiveness in controlling dental caries. The program for fluoridation of public water supplies deficient in natural fluorides has been sponsored by many organizations interested in public health, such as the American Dental and Medical Associations. The process of fluoridation is now practiced in approximately 5,000 communities, serving over 80 million persons.¹

FLUORIDATION

Fluorine is the most chemically active element known. Like chlorine, it is never found in a free state, but always occurs in combination with other elements, in fluoride compounds. In water solution, the compounds dissociate into ions, the form in which fluorine is assimilated by humans. Theoretically, any compound that gives fluoride ions in water solution can be used for increasing the fluoride content of a water supply. However, there are several practical considerations involved in selecting the fluoride source. First, it must be sufficiently soluble to be used in routine water practice. Second,

the compound must not have any undesirable characteristics. Third, the material used should be readily available and relatively inexpensive.

The three most commonly used fluoride compounds in water treatment are sodium fluoride (NaF), sodium silicofluoride (Na_2SiF_6), and fluosilicic acid (H_2SiF_6). Other compounds used for fluoridation include calcium fluoride (CaF_2), ammonia silicofluoride ($(\text{NH}_4)_2\text{SiF}_6$), and hydrofluoric acid (H_2F_2). The most commonly used compounds will be described in detail.

Sodium Fluoride

Sodium fluoride (NaF) was the first fluoride compound used for fluoridation. Although it is one of the most expensive fluoridation compounds for the amount of available F, it is still the most widely used.

NaF is a white, odorless material available either as a powder or in crystalline form. Table 20-2 lists the characteristics of NaF and the other two popular fluoridation compounds. The maximum solubility of NaF is 4.0 percent, resulting in a fluoride concentration of 18,000 mg/l. Its solubility is practically constant over the temperature range generally encountered in water treatment. Solution pH varies with the type and amount of impurities, but solutions prepared from the usual grades of NaF exhibit near-neutral pH.

Powdered NaF is produced in densities ranging from 65 to 90 pounds per cubic foot (1,054 to 1,458 kg/m³). Crystalline NaF is produced in various size ranges, usually designated as coarse, fine, and extra-fine. The crystalline form is preferred when manual handling is involved because the absence of fine powder results in a minimum of dust.

Table 20-2. Characteristics of Fluoride Compounds.

ITEM	SODIUM FLUORIDE, NaF		SODIUM SILICOFLUORIDE, Na_2SiF_6		FLUOSILICIC ACID, H_2SiF_6	
	Powder or crystal	Crystal	Powder or very fine crystal	Crystal	Liquid	Liquid
Molecular weight	42.00		188.05		144.08	
Commercial purity, %	90-98		98-99		22-30	
Fluoride ion, % (100% pure material)	45.25		60.7		79.2	
Lb (kg) required per MG (Ml) for 1.0 mg/l F at indicated purity	18.8 (2.25) (98%)		14.0 (1.68) (98.5%)		35.2 (4.22) (30%)	
pH of saturated solution	7.6		3.5		1.2 (1% solution)	
Solubility, g per 100 g water, at 25°C	4.05		0.762		Infinite	

Sodium Silicofluoride

Sodium silicofluoride (Na_2SiF_6) is the cheapest of the compounds currently in use. Its cost makes it very popular for use in fluoridation.

Na_2SiF_6 is a white, odorless crystalline powder. Its solubility varies from 0.44 percent at 32°F (0°C) to 2.45 percent at 212°F (100°C). Saturated solutions exhibit an acid pH, usually between 3.0 and 4.0. The density of Na_2SiF_6 ranges from 55 to 72 lb/cu ft (892 to 1,167 kg/m³). Experience has shown that for best feeding results with mechanical feeders, the Na_2SiF_6 should have a low moisture content plus a relatively narrow size distribution.

Fluosilicic Acid

This fluoridation compound is a 20 to 35 percent solution of H_2SiF_6 in water. When pure it is a colorless, corrosive liquid with a pungent odor and can cause skin irritation. Upon vaporizing, the acid decomposes to form hydrofluoric acid and silicon tetrafluoride. All solutions of fluosilicic acid are characterized by a low pH. A concentration sufficient to produce 1 mg/l of fluoride ion can cause a significant pH depression in poorly buffered waters. For example, in water at pH 6.5 and containing 30 mg/l of total dissolved solids (TDS), the addition of H_2SiF_6 to produce 1 mg/l of fluoride ion caused the pH to drop to 6.2.¹

Fluosilicic acid is a solution containing a high proportion of water. Consequently, large quantities can be expensive to ship. Economics generally restricts fluoridation by fluosilicic acid to the smaller waterworks.

Other Fluoride Compounds

Calcium fluoride (CaF_2), ammonium silicofluoride ($(\text{NH}_4)_2\text{SiF}_6$), and hydrofluoric acid (H_2F_2) have been used for water fluoridation. Each has particular properties that make the compound desirable in a specific application; however, none has widespread use.

Fluorspar (CaF_2) is the cheapest of the compounds used for fluoridation, but it has the disadvantage of being the least soluble. It has been successfully fed by first dissolving it in an alum solution, and then utilizing the resultant liquid to supply both the alum needed for coagulation and the fluoride for fluoridation. Some attempts have been made to feed fluorspar directly in the form of ultra-fine powder, on the premise that the powder would eventually dissolve or would remain in suspension until consumed.

Ammonia silicofluoride ($(\text{NH}_4)_2\text{SiF}_6$) has the advantage of supplying the ammonium ion necessary for the production of chloramines when this form of disinfectant is preferred to chlorine. Otherwise, it has found little use in fluoridation.

Hydrofluoric acid (H_2F_2) has been used in a few specially designed installations. It is low in cost, but it presents a safety and corrosion hazard and is generally not used for fluoridation.

FLUORIDATION SYSTEMS

No one type of fluoridation system is applicable to all water treatment plants. Selection is based on size and type of water facility, chemical availability, cost, and operating personnel available. For small utilities, usually some type of solution feed is selected, and batches are manually prepared. A simple system consists of a solution tank and a solution metering pump with appropriate piping from the tank to the water main for application (Fig. 20-2). If fluosilicic acid is used, it is either used at full strength (Fig. 20-3) or diluted with water in the feed tank (Fig. 20-4). When sodium fluoride is used, the feed solution may be prepared to a desired strength or as a saturated solution. Because NaF has a maximum solubility of 4.0 percent, a saturated solution is prepared by passing water through a bed containing an excess of NaF (Fig. 20-5). While NaF is quite soluble, calcium and magnesium fluorides form precipitates that can scale and clog feeders and lines. Consequently, dis-solution water should be softened whenever the hardness exceeds 75 mg/l.

Large waterworks usually use either gravimetric dry feeders to apply sodium silicofluoride (Fig. 8-13) or solution feeders to apply fluosilicic acid. Often their systems incorporate automatic control systems to regulate flow

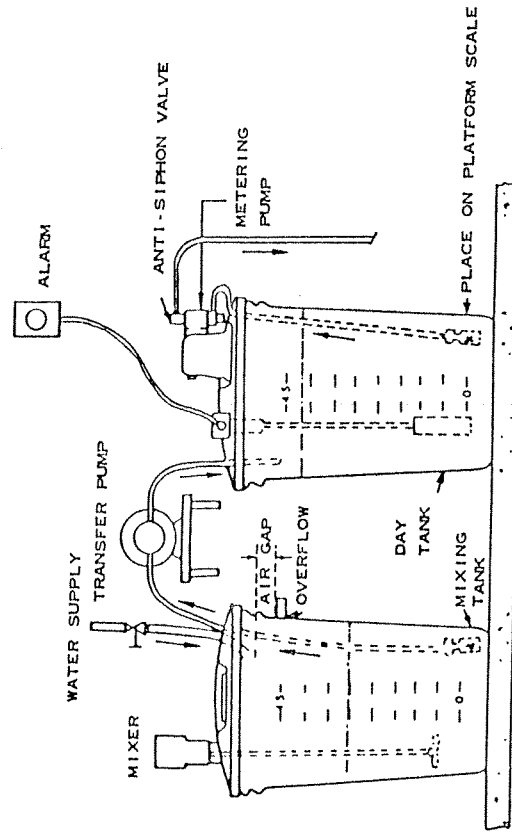


Fig. 20-2. Solution feed installation.

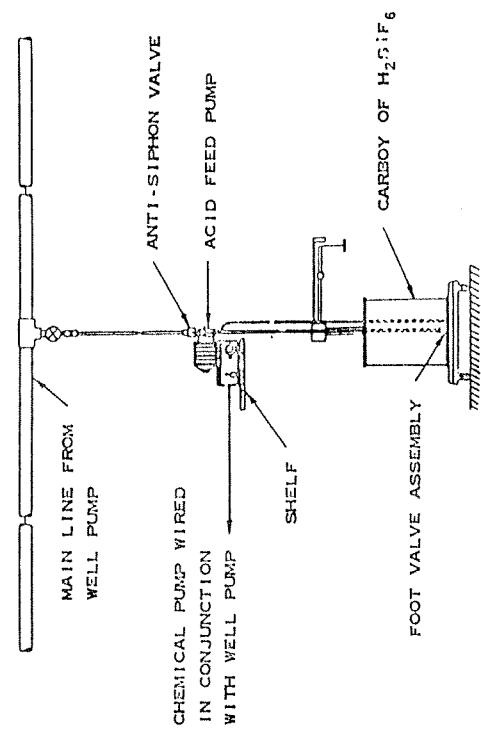


Fig. 20-3. Acid feed installation.

and adjust feed rates. Fluoride feed must be paced to water flow to maintain a consistent fluoride ion concentration.

Fluoride must be injected into all of the water entering the distribution system. If there is more than one supply point, separate fluoride feeding installations are required for each water facility. In a well system, application

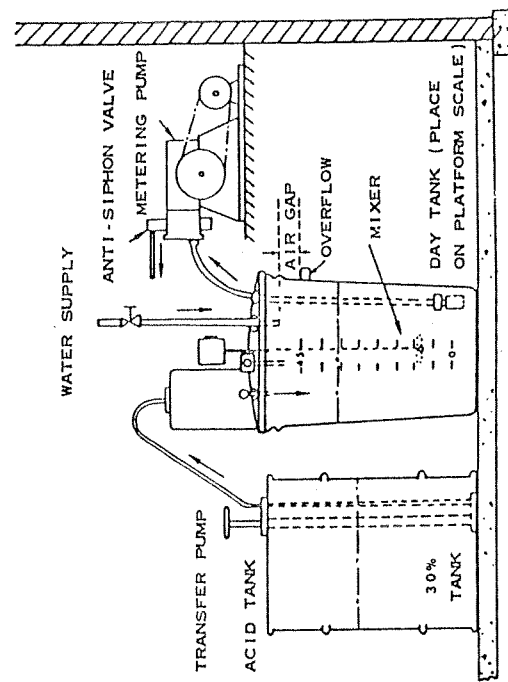


Fig. 20-4. Diluted acid feed system.

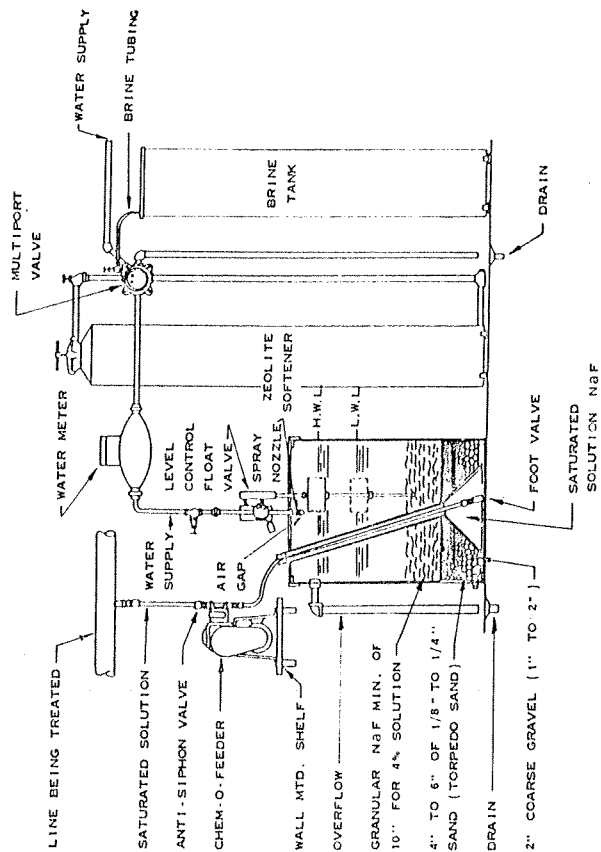


Fig. 20-5. Downflow saturator.

can be in the discharge line of each pump or in a common line leading to a storage reservoir. Fluoride can be applied in a treatment plant in a channel or line from the filters, or directly into the clearwell. Whenever possible, it should be added after filtration to avoid possible losses due to reactions with other chemicals. Of particular concern are coagulation with alum and lime-soda softening. Fluoride injection points should be as far away as possible from the addition of chemicals that contain calcium because of the insolubility of CaF.

Surveillance of water fluoridation involves testing both the raw and treated water for fluoride ion concentration. Records of the weight of chemical applied and the volume of water treated should be kept to confirm that the correct amount of fluoride is being added. The fluoride concentration in the treated water should be that recommended by drinking water standards (Table 20-1).

DEFLUORIDATION

As soon as excessive amounts of fluorides in drinking water supplies had been established as the cause of dental fluorosis, methods for their removal were studied. Comparatively little research has been performed on theoretical

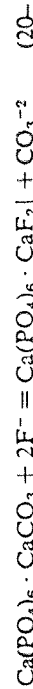
design models for the removal of fluorides. Consequently, the design of defluoridation processes is largely based on past experience and empirical models. Fluoride removal is complicated by the presence of other ions in the water that compete with fluoride for removal. The design of defluoridation systems requires laboratory- and pilot-scale work prior to the design of full-scale treatment systems.

Two methods of defluoridation have found practical application. One involves passage of water through defluoridation media such as bone meal, bone char, ion-exchange resins, or activated alumina. The second involves the addition of chemicals such as lime or alumina prior to rapid mixing, flocculation, and sedimentation in a waterworks, for the removal of fluoride only or the concurrent removal of fluoride and other ions (e.g., calcium and magnesium removal for water softening).

The following discussion presents past experience with media filter and chemical addition defluoridation systems.

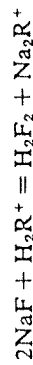
Defluoridation Media

The uptake of fluoride onto the surface of bone was first reported by Smith and Smith in 1937.⁹ They suggested that fluoride was removed by ion exchange in which the carbonate radical of the apatite comprising bone [$\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3$] was replaced by fluoride to form an insoluble fluorapatite according to:



Similarly, bone char or tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), produced by carbonizing bone at temperatures of 2012 to 2912°F (1100 to 1600°C), has been used for defluoridation. When exhausted, the column is regenerated by application of a 1.0 percent solution of caustic soda, which converts the fluorapatite to hydroxyapatite ($\text{Ca}(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$). The fluoride is removed as soluble sodium fluoride. The caustic is followed by a rinse, and then a acid wash to lower the pH.¹⁰ In the regenerated form, the hydroxyl radical becomes the exchange anion in the defluoridation reaction.¹¹ Bone char has been used successfully for full-scale defluoridation.¹²

Paired cationic and anionic exchange resin beds have also been used for defluoridation. In this process, illustrated by Fig. 20-6, water first passes through a cationic resin (R^+) bed, which exchanges sodium with hydrogen to form the equivalent acid:



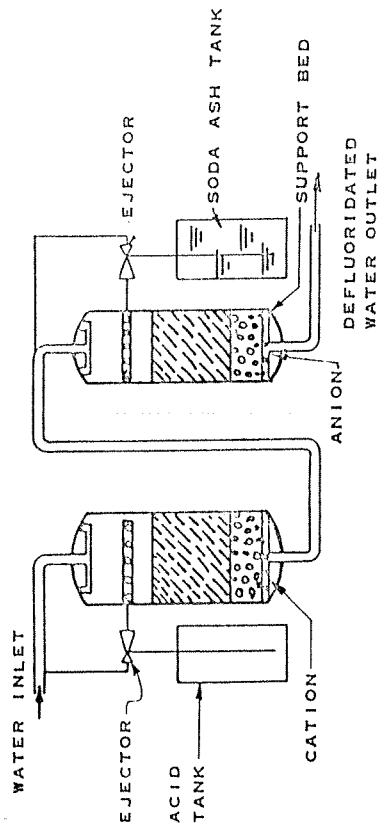


Fig. 20-6. Paired cationic and anionic exchange resin beds for fluoride removal.

The hydrogen fluoride is then removed during passage through the anionic bed (R^-):



Periodically, the resins are regenerated with acid and alkaline solutions. Synthetic ion exchange resins for defluoridation are available from several manufacturers.

The most widely used defluoridation method involves beds of granular activated alumina (Al_2O_3). Some researchers have concluded that defluoridation by activated alumina is the result of ion exchange.¹³ However, Wu and Nitya recently showed that the process is one of adsorption and follows the Langmuir isotherm.¹⁴

An example of fluoride removal by activated alumina is the plant at Gila Bend, Arizona, which has been in operation since 1978. This plant has a treatment capacity of 0.625 mgd (2.37 MI/d), and has successfully reduced raw water fluoride levels of 3.0 mg/l to as low as 0.1 mg/l. The plant consists of two 10-foot (3.05-m)-diameter, rubber-lined vertical pressure vessels, each containing 5 feet (1.5 m), or 380 cubic feet (10.8 m³), of Alcoa F-1 (-28, +48 mesh) activated alumina. Operation consists of adjusting the raw water pH to 5.5 with sulfuric acid prior to treatment, and after treatment, pH adjustment to 7.4 with 50 percent sodium hydroxide. Careful raw water pH control is necessary because of sensitivity of the fluoride removal reaction to pH. Experienced exchange capacities have ranged between 2,000 and 4,000 grains/cu ft (70.7 and 141.4 kilograms/m³), depending upon raw water pH and fluoride concentration. The plant was designed for operation between 5 and 7.5 gpm/sq ft (12.2 and 18.3 m³/h). Treatment runs for each exchanger are between 3.5 and 5 MG (13.3 and 18.9 MI), and treated water is blended

in a storage tank to produce a water with 1.0 mg/l of fluoride for distribution. Regeneration consists of three steps: backwash, regeneration, and neutralization. Backwashing with raw water is performed at a rate of 8 to 9 gpm/sq ft (19.5 to 22 m³/h), which expands the bed by 50 percent. The purpose of backwashing is to remove suspended solids that have been filtered from the water and to unpack the bed, thus preventing tendencies toward channeling. Backwashing normally takes 10 minutes.

Regeneration is initiated while the bed is still expanded, by employing a 1 percent sodium hydroxide solution at a rate of 2.5 gpm/sq ft (6.1 m³/h), followed by an upflow rinse at a rate of 5 gpm/sq ft (12.2 m³/h) for 30 minutes. Next, the unit is drained to the top of the treatment bed, and downflow regeneration with a 1 percent sodium hydroxide solution is performed at the same flow rate as the upflow regeneration for 35 minutes.

The bed pH will be 12 to 13 as a result of the NaOH treatment. Wu and Nitya demonstrated that fluoride removal by activated alumina is strongly pH-dependent, with little removal occurring at pH values above 11 and optimum removal occurring at pH 5 (Fig. 20-7).¹⁴

Prior to neutralization, the unit is drained to the top of the bed, and raw water is adjusted to pH 2.5 and is fed downflow at the normal treatment rate of 5 to 7.5 gpm/sq ft (12.2 to 18.3 m³/h). As the fluoride level in this water drops below the required level, the water is diverted to storage, and is neutralized by water being treated by the second unit.

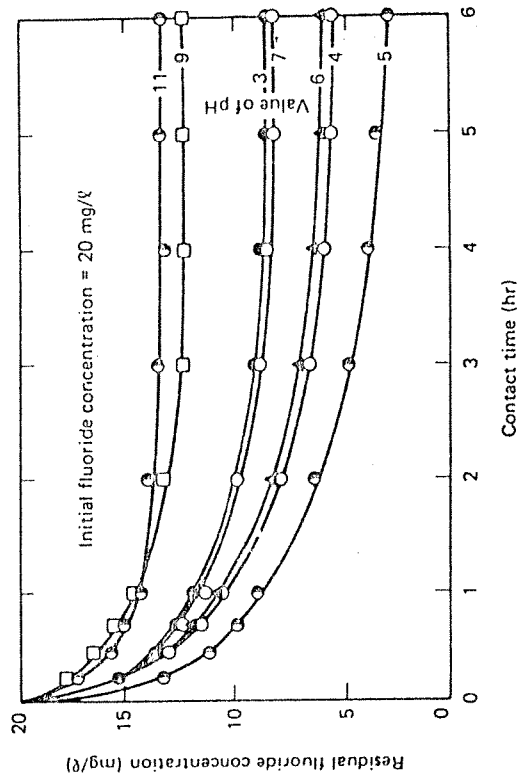


Fig. 20-7. Effect of pH and time of contact on fluoride removal of activated alumina adsorption.¹⁴

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"Chapter 21" - Lime-soda softening