

EFFECTS OF WATER COMPOSITION
ON FLUORIDE REMOVAL

by

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ABSTRACT

The effects of water composition as they apply to the design of virgin and regenerated activated alumina and virgin and regenerated bone char defluoridation units were studied. Freundlich isotherm analysis was used to determine the degree of the effect compared to an arbitrary standard.

The results showed that ionic strength, divalent metal ions, arsenic, and pH connected to buffering capacity have significant effects. The anions sulfate, nitrate, and chloride showed negligible effect on the removal of fluoride.

CHAPTER 1

INTRODUCTION

Dental fluorosis or mottled enamel is a disfigurement of the teeth caused by a high intake of fluoride ion through food or water by an individual during development of teeth. This defect has been variously described as Denti di Chiaie (Chiaie teeth) (1), endemic dental fluorosis (2), and as objectionable dental fluorosis (3). The term dental fluorosis will be used to refer to the defect throughout the remainder of this investigation.

The first formal report of dental fluorosis was made by Professor Stefano Chiaie, a Neapolitan, to the Surgeon General of the Public Health Service on October 7, 1901 (1). Conclusive proof of the cause of dental fluorosis was presented by Smith, Lantz, and Smith (4) in 1931. A series of articles published in Fluoride Drinking Waters (5) describes the studies which contributed to the isolation of the age brackets at which humans who ingest fluoride are affected, and the concentrations which cause the defects. It was shown that only developing teeth were mottled and that mature teeth were not disfigured. Furthermore, it was found that approximately 1 ppm (mg/l) of fluoride would

inhibit formation of dental caries in both developing and mature teeth. With this knowledge, the United States Department of Health, Education and Welfare, Public Health Service, presented the standards in Table I for fluoride concentrations in drinking waters (6).

Another human disease, fluoride osteosclerosis, can result from the ingestion of excessive fluoride over a long period of time. This condition of bone hardening was shown to be linked to fluoride by Linsman and MacMurray (7). They suggested that populations in areas where fluoride content of drinking waters exceeds 3 mg/l should be

TABLE I
RECOMMENDED CONTROL LIMITS FOR FLUORIDE CONCENTRATION
AS A FUNCTION OF AIR TEMPERATURE

Annual Avg. of max. daily air temp., °F	Recommended control limits for fluoride concentration, mg/l			Mandatory Rejection Limit mg/l
	Lower	Optimum	Upper	
50.0 -53.7	0.9	1.2	1.7	2.4
53.8 -58.3	0.8	1.1	1.5	2.2
58.4 -63.8	0.8	1.0	1.3	2.0
63.9 -70.6	0.7	0.9	1.2	1.8
70.7 -70.6	0.7	0.8	1.0	1.6
79.3 -90.5	0.6	0.7	0.8	1.4

studied by public health authorities to determine how widespread the condition of osteosclerosis is. Evidence indicates that osteosclerosis may give rise to anemia and subsequent kidney damage.

It is with this motivation that this research was undertaken.

Sources of Fluoride in Water

Fluoride is a constituent of igneous and sedimentary rocks with an average of 290 ppm in the 10 mile deep earth's crust. It is contained in varying amounts in the following minerals: fluorite (fluorspar), apatite, cryolite, biotite, muscovite, hornblende, topaz, phlogopite, lepidolite, and zinnwaldite (8, 9). Complete elemental compositions of various rock types are presented by Hem (10).

The natural weathering and dissolution of such minerals is the primary natural source of fluoride in the aqueous environment. However, not all of the fluoride in drinking waters is of natural origin. Phosphate rock processing plants have wastewaters with very high fluoride concentrations. The nature and location of these discharges are such that underground as well as surface waters can be affected (11). It is also recognized that fluoride can get into drinking water supplies via the application of

fluoride containing phosphate fertilizers to agricultural land (12).

Geographical Location of Fluoride Waters

Many water supplies in the United States have fluoride concentrations in excess of the mandatory rejection limit of the U. S. Public Health Service. Areas where high fluoride supplies are found are described by Maier (13). There are 4.1 million people living in 1,200 communities where water supplies contain fluoride in excess of the optimum. Dutt and McCreary published data on individual wells throughout Arizona and have mapped areas of adverse fluoride concentrations (14). Smith, et al. (15) published a survey of the water quality of Arizona's domestic waters including fluoride concentrations in 1963.

Future water demands will require the utilization of more supplies containing high fluoride concentrations. There is also the possibility that water reuse will result in a build-up of fluoride in waters.

Objective

The objective of this thesis is to determine the quantitative effects of water composition on the removal of fluoride from aqueous solutions by sorption processes. In the literature, there is very little fluoride removal data available other than information from a few operating plants. The choice of sorption media for fluoride removal by

designers has been made on a basis of documented success. Adsorption isotherms are used in this study to determine the comparative degrees of removal of fluoride by different media from waters of various compositions. Agreement between known plant performance and these laboratory studies will be presented.

Scope

Activated alumina and bone char (animal charcoal or bone black) were selected as defluoridation media for use in these experiments on the basis of past engineering experience. Virgin and regenerated media will be investigated. Virgin media have application in single pass disposable units. Regenerated media are used in large municipal installations where virgin media is uneconomical to use. Synthetic tricalcium phosphate and synthetic hydroxyapatite have been investigated in a study (16) which was parallel to the present work and thus were not chosen. Activated carbon also has been tried, but limited ranges and low sorption capacity economically eliminates it from use with drinking waters (17).

In light of the fact that production of potable water was the ultimate goal of this study, only waters with total dissolved solids of less than 1000 mg/l were considered. The complete removal of fluoride from a water with total dissolved solids greater than 1000 mg/l does not

result in a potable water (6). The 1000 mg/l TDS criteria was used to select groundwater quality input data for determining typical compositions of water with high fluoride concentration.

CHAPTER 2

THEORY OF FLUORIDE REMOVAL WITH VARIOUS MEDIA

Early defluoridation methods were based on the fact that bone has an affinity for fluoride. Synthetic hydroxy apatites and calcium phosphates having chemical compositions similar to bone were also successfully applied to the problem. Activated alumina was found to remove fluoride. Activated carbon was tried as a removal medium but found to be uneconomical. Several precipitation reactions involving calcium, magnesium, and aluminum salts were found to remove fluoride. Total deionization and partial selective deionization by various media are also applicable to defluoridation.

This chapter describes the theory of the physical and chemical phenomena of fluoride removal. Individual reactions and mechanisms will be described in detail. Thermodynamic considerations will be presented to elucidate certain reactions.

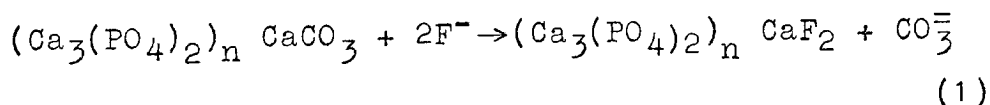
Calcium Phosphates

Smith and Davey (18) conducted a study on the practicality of using bone for fluoride removal. While they found bone to be an acceptable and economical media for

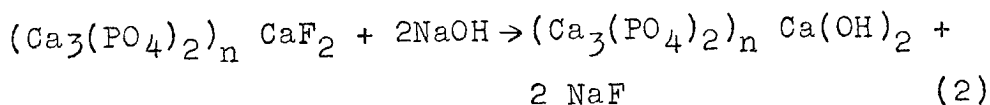
fluoride removal, they were not able to define the mechanism of the removal reaction.

Adler, Klein, and Lindsay (16) performed laboratory column studies with tricalcium phosphate. They found removal capacities of 3.6 to 3.8 gm F per kg of tricalcium phosphate when treating a 30 mg/l fluoride water. Increased hardness of the water decreased capacity of the media from 3.7 gm/kg at 51 mg/l of hardness (as CaCO_3) to 2.9 gm/kg at 260 mg/l. The removal mechanism was assumed to be adsorption, but in light of the composition of tricalcium phosphate, formation of a complex compound such as fluorapatite would also explain fluoride removal. Regeneration with caustic followed by acid neutralization caused a 2.5 - 3.0% weight loss of the media per regeneration due to the dissolution of the media in acid solution.

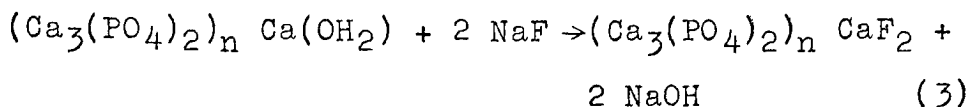
Maier (19) proposes an ion exchange mechanism for fluoride ion removal by calcium phosphate (apatite) which is described by the following reaction:



Regeneration with caustic soda proceeds by:



The regenerated material exchanges hydroxyl for fluoride in the reverse of reaction expressed in equation (2) going from fluorapatite to hydroxy apatite.



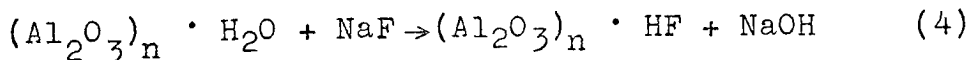
Goodwin and Litton (20) reported promising results for a specially prepared mixture of calcium phosphate monohydrate and hydroxyapatite, $\text{Ca}_3\text{P}_2\text{O}_8\text{Ca}(\text{OH})_2$. They suggested that an ion exchange of hydroxyl for fluoride produces a fluorapatite. Regeneration with caustic replaces the fluoride with hydroxyl.

Bone char (animal charcoal, bone black) is composed of the hydroxy apatite of the bone plus carbon formed in the combustion of the bone during manufacture (19). The active hydroxy apatite portion behaves according to the equation 1.

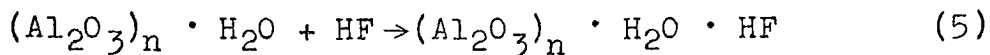
Caustic soda of the calcium phosphate medium is usually followed by an acid rinse to remove residual caustic. Behrman and Gustafson (21) have developed a carbonic acid (dissolved CO_2) method for neutralizing excess residual caustic which prolongs the active life of both tricalcium phosphate and hydroxy apatite.

Aluminum Compounds

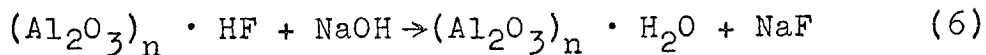
Activated alumina acts as a sorption medium or ion exchanger for fluoride. A possible reaction in the pH range of potable waters is:



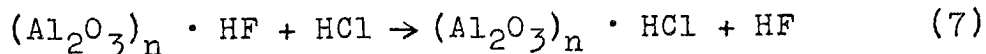
If the pH is below 4, the dominate fluoride species is HF and the following reaction may apply:



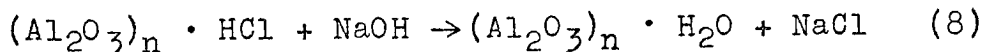
Regeneration of the spent medium can be accomplished by exposure to either acidic or basic solutions. Caustic regeneration of the spent media $(\text{Al}_2\text{O}_3)_n \cdot \text{HF}$ from equation (3) is described by



Acid regeneration of the same media proceeds by:



Caustic neutralization of the $(\text{Al}_2\text{O}_3)_n \cdot \text{HCl}$ produced in reaction 7 replaces the hydroxyl on the alumina according to



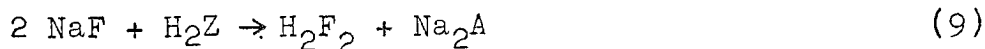
The possibility remains that an aluminum fluoride complex is formed at the activated aluminum surface. However, laboratory experiments and field experience indicate that regeneration renews the capacity for fluoride sorption. The complex must therefore be broken up.

Research has shown other aluminum salts also to be effective in removing fluorides. Most notable among these compounds are aluminum sulfate and aluminum hydroxide. They can be used in combination with other insoluble compounds in contact beds or as constituents of floc which is later removed by sedimentation and/or filtration. Fluoride removal can be due to either the formation of an insoluble aluminum fluoride complex or to sorption of the fluoride ion onto the media or floc (19).

Savinelli and Black (22) investigated laboratory test columns of activated alumina regenerated with alum solutions. They believe the removal reaction to be one of ion exchange. They also found that the capacity of the media is reduced by high alkalinities and high pH's.

Ion Exchangers

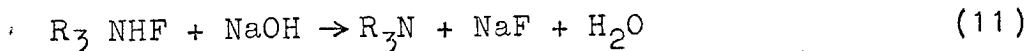
Reactions involving ion exchange were the basis of a system proposed by Behson, Porth, and Sweeney (23). Their system involved a cation exchanger (Zeo-Karb H of the Permutit Corporation) followed by an anion exchanger (Nalcite B supplied by the National Aluminate Corporation). In the first step alkali metals are replaced with hydrogen by:



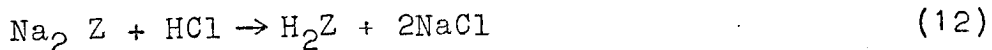
where Z represents the exchange material. Effluent pH being quite low results in formation of H_2F_2 (or HF). The second reaction is:



where R_3N represents the resin. Regeneration of the anion exchanger is accomplished by contact with soda solutions:



Acid solutions are used to regenerate the cation exchange resin:



Mixed bed ion exchangers used for total deionization remove essentially all fluoride as well as all other ions.

Activated Carbon

Defluoridation with activated carbon was studied by McKee and Johnston (17). They were successful in their attempts using an acid activated residual carbon discarded by the soda pulp industry. The drawback of the method is that fluoride removals from 10 ppm to below 1.0 ppm could be achieved only at pH 3 or lower. No removal mechanisms were presented. However, the thermodynamics of a pH 3 or less system is such that the fluoride is in the HF form and is amenable to adsorption as HF. See Appendix B.

Other Compounds

Boruff (24) conducted tests on several media to determine their efficiency in removing fluoride. The following were examined: aluminum sulfate, sodium aluminate, zeolite, alumina, bauxite, silica gel, sodium silicate, ferric salts, and lime treatment. The application of his results to water supplies is complicated by the fact that he used a synthetic water containing 330 ppm of carbonate in addition to normal amounts of other salts found in waters.

Surface Properties of Media

The surface of the bone char is probably some combination of oxygen in the apatites and carbon. Just the ratio of oxygen to other elements points to the probability of the surface of apatite being oxygen. The surface of dry

activated alumina is known to be an orderly lattice of oxide ions which are part of the structure of the compound. Hydrated alumina has a surface composed of hydroxide ions with twice the number per unit area as compared to the oxide ions of the dehydrated state. In hydration, water molecules attach to the surface and dissociate to provide each oxide ion with a hydrogen (25). Because of its surface properties, dry activated alumina is very hydroscopic. Exposure to the laboratory atmosphere for the short period of time required for mass measurement caused a noticeable increase in weight. Some error is therefore inherent in measurements of mass for the media.

CHAPTER 3

ENGINEERING PRACTICE IN FLUORIDE REMOVAL

Several defluoridation plants are in existence in the United States. A review of these installations is necessary to illustrate the range of application of the known removal processes and the related theory, and to present the background information on the known effects of water composition on fluoride removal.

Application of Bone Char

The Britton, South Dakota plant is the most well known of those using bone char. The defluoridation unit is a 9 ft (2.73 m) diameter by 10 ft (3.04 m) high steel tank containing $56\frac{1}{2}$ in. (143.5 cm) (300 ft^3) of 28 x 48 standard sieve size bone char. The bulk density of the media in place is 50 lb/ft^3 (802 kg/m^3). Twelve in. (30.5 cm) of graded gravel supports the media. Flow rates vary from 38 to 206 gpm (144 to 780 l/min). The concentration of fluoride is reduced from 8.0 mg/l to 1.0 mg/l averaged over a run of about 450,000 gal (1680 m^3) between regenerations.

Regeneration is accomplished by a caustic wash. First the column is backwashed with treated water at 370 gpm (1400 l/m) for 18 minutes. Next, 5,000 gal (18.9 m^3) of 1%

caustic soda is applied at 150 gpm (567 l/m). Caustic is washed out with 7000 gal (26.5 m³) of raw water pumped at 150 gpm (567 l/m). A weak CO₂ solution is used to neutralize the residual caustic. The weak acid is made by diffusing 84 lb (41.6 kg) of CO₂ gas through 8,500 gal (32.2 m³) of raw water as it is transferred to the column at 150 gpm (567 l/m). A total of 6,500 gal (24.6 m³) of treated water and 28,000 gal (106 m³) of raw water is used in regeneration.

When a water supply containing a lower concentration of fluoride (3.0 mg/l) was applied to the column, runs between regenerations increased to 1.5 mil gal (56,700 m³). Because of the smaller driving force of fluoride, the media capacity dropped to 400 gr/ft³ (1.14 gm/kg) from 700 gr/ft³ (2.00 gm/kg) with the 8.0 mg/l water (26, 27).

Application of Activated Alumina

The Bartlett, Texas plant is the outstanding example of the use of activated alumina. The plant serves a population of 1,760. The unit is an 11 ft (3.34 m) diameter by 11½ ft (3.49 m) high steel tank with a steel pipe grid underdrain and a 4 in. (10.2 cm) plastic acid and caustic distributor. Sixty in. (1.82 m) (500 ft³ (14.2 m³)) of 28 x 48 standard sieve size activated alumina is supported by 12 in. (30.5 cm) of graded gravel. The average flow rate is 400 gpm (1890 l/m). Fluoride concentration is reduced

from 8.1 mg/l to 1.0 mg/l over a run of from 400,000 to 500,000 gal (1410 to 1890 m³) between regenerations. The removal capacity is 700 grains/ft³. For a bulk media density of 56.5 lb/ft³, the capacity is 1.77 gm/kg.

Regeneration requires four steps. First, the media is backwashed with 5000 gal (18.9 m³) of 1% sodium hydroxide at 235 gpm (914 l/m). Second, about 28,000 gal (106 m³) of raw water is used to wash out the caustic. Third, 15,500 gal (58.6 m³) of 0.05 N sulfuric acid is applied. Fourth, a final rinse of 25,000 gal (94.6 m³) of raw water restores the media to a useable condition. Regeneration water usage is 73,500 gal (278 m³) of raw water (28, 29).

The activated alumina plant in Elsinore, California, treats a water of pH 9.9. Pretreatment with acid reducing the pH to 7.4 results in a 125% increase in the length of the run to exhaustion (3).

Harmon and Kalichman (3) reported on the plants in existence in Southern California. These include all types of solid media in units of several sizes serving single dwellings to small communities. The Camp Irwin, California plant is discussed in more detail in an article in Public Works (30).

Fink and Lindsay (31) developed an activated alumina unit for use in individual households. It contained 9.75 lb (4.42 kg) of alumina in a bed 6 in. (15.2 cm) deep. Two hundred fifty gal (946 l) of 5.0 mg/l fluoride water could

be treated at 0.4 gpm (1.5 l/m) before the effluent concentration of fluoride reached 1.0 mg/l.

Precipitation Methods

Culp and Stolenberg (32) designed a plant for LaCrosse, Kansas, using alum flocculation. The supply to be treated was a soft, highly mineralized water containing 3.6 mg/l fluoride. From 225 to 315 mg/l of alum was to be added to the water. Chlorine was to be added to oxidize excessive concentrations of dissolved iron. Following a rapid mix, the water would be flocculated for 30 minutes. From 15 to 20 mg/l of lime was to be necessary for pH control. A 2 to 4 hour sedimentation period followed by rapid sand filtration was to produce a desirable effluent.

Finkbeiner (33) reported the reduction of fluoride from 2.2 mg/l to 1.2 mg/l by lime-soda softening of water containing considerable magnesium in the Bloomingdale, Ohio plant.

CHAPTER 4

METHODS AND PROCEDURES

Chemical analysis made in this study were performed according to the procedures described here. All chemicals used were American Chemical Society reagent grade except where noted.

Laboratory Procedures

Fluoride determinations were made with a modification of the electrode method of Standard Methods (34) suggested by Warner (35). The apparatus used was a Beckman Selection 39600 FLUORID specific ion electrode coupled with a Beckman 39402 A-2 reference electrode. Comparative millivolt readings were determined with a Beckman Expandomatic pH - millivolt meter. Solutions were agitated with teflon covered stirring magnets. Standard (1.00 ml = 10.0 ug F) and stock (1.00 ml = 10 ug F) solutions of fluoride and total ionic strength adjustment buffer (TISAB) were prepared according to Standard Methods (34).

A series of valibration standards for fluoride in the range of 0.10 to 10.0 mg/l were prepared. Fifty ml of each standard was pipetted into a 150 ml beaker along with 10.00 mg/l TISAB. The meter was adjusted to read 100 at

1.0 mg/l sample plus buffer. A typical calibration curve is illustrated in Appendix C. On a day to day basis, 1.0 and 10.0 mg/l F^- standards were prepared by adding 10.00 ml TISAB to 50.00 ml of solution. Samples were prepared likewise. Millivolt readings were taken after a $2\frac{1}{2}$ to 3 minute stabilization period. Fluoride concentrations were interpreted from the calibration curve.

All pH measurements were made with a Beckman Expandomatic meter, a standard saturated KCl calomel reference electrode and a Beckman #41263 pH electrode. Calcium concentrations were measured by the EDTA titrametric method described in Standard Methods.

Fines were removed from virgin 28 x 48 mesh activated alumina (Alcoa grade F 1) by washing with distilled water through a 60 mesh sieve. The alumina was placed in beakers and dried at $103^{\circ}C$ for 20 or more hours. After cooling in a desiccator, the samples were sealed in screw capped glass bottles for storage.

Granular bone char (Van Waters and Rogers Bone Charcoal, Technical grade) was ground with a mortar and pestle, fractionated to 28 x 60 mesh, washed on a 60 mesh sieve, dried at $103^{\circ}C$ for 20 or more hours, and cooled in a desiccator. Samples were stored in screw capped glass bottles.

Regeneration

Regeneration procedures were based on operational data from the plants at Bartlett, (28, 29) and Britton, (26, 27). Table II shows the concentrations and amounts of regenerant, rinse, and neutralizer used for each of the media. Dilute HCl was used in place of the carbonic acid since attrition of the material was not investigated. The volumes of bone char and activated alumina regenerated were 0.31 and 0.61 l, respectively.

TABLE II
TABLE OF REGENERATION CHEMICALS

	Bone Char Conc	l	Activated Alumina Conc	l
Caustic (NaOH)	1% w/w	0.7	8% w/w	0.8
Rinse, Distilled		0.9		4.4
Acid (HCl)	0.02 N	1.2	0.05 N	2.4
Rinse, Distilled		1.5		4.0

Regeneration was carried out in an Erlenmeyer flask of sufficient size to hold the spent medium and approximately half of the caustic volume. After sufficient detention times, i.e., 20 min for the caustic and 10 min for the acid neutralizer, the spent solutions were decanted.

After regeneration, the medium was dried and stored. Resaturation of the medium with fluoride to produce a

multiply regenerated medium was accomplished by exposing the medium to sodium fluoride solution. Concentration of medium and fluoride were chosen so that the equilibrium X/M value was of the same magnitude as the X/M values of the raw media experiments (see section on isotherm analysis in this chapter).

Computer Study

A computer was used to determine typical compositions of natural ground waters having high fluoride concentrations. The data of Dutt and McCreary (14) for subsurface waters from all of Arizona except Maricopa County were used to determine concentration means and standard deviations of the major components of waters with fluoride concentrations greater than 1.4 mg/l and total dissolved solid concentrations of less than 1,000 mg/l. See Table III. Only those waters having total dissolved solids concentrations less than 1,000 mg/l were considered since the object of this study is to reduce fluoride concentrations in potable waters. Tables of average water compositions, correlations of components, and a description of the program are presented in the Appendix.

Isotherm Analysis

Adsorption isotherms were determined by placing various known masses of media in a series of flasks containing known volumes of water with known concentrations

TABLE III

MEANS AND STANDARD DEVIATIONS OF COMPONENTS OF ARIZONA
WATERS WITH $F^- \geq 1.4$ mg/l AND TDS ≤ 1000 mg/l

Component	Mean mg/l	Standard Deviation mg/l
Calcium	36.4	31.7
Magnesium	9.0	8.4
Sodium	107.5	64.3
Chloride	75.4	78.1
Sulfate	112.9	83.1
Bicarbonate	166.1	75.7
Carbonate	2.2	5.1
Fluoride	4.1	3.8
Nitrate	4.8	6.2
pH	8.0	0.6
Potassium	3.9	3.2
Boron	.4	.9
Silicon (SiO_2)	22.8	12.2

of fluoride and other water components. The media and fluoride solution was mixed for two hours on a gyratory shaker table. Kinetic experiments showed that the regenerated activated alumina achieved sorption equilibrium in 15 minutes. Regenerated bone char attained about 95% of equilibrium saturation in 2 hours.

The fluoride removal data were analyzed using the Freundlich isotherm relationship.

$$X/M = kc^{1/n}$$

where X = weight of material removed (mg)

M = weight of the media (grams)

C = equilibrium concentration of the residual fluoride ion (mg/l)

k, $1/n$ = constants for each particular system

Log-log plots of X/M in mg/gm (gm/kg) versus the equilibrium concentration of fluoride were made (36). The constants k and $1/n$ were not determined since only the comparative effects were desired. The precedent for this procedure in analysis of fluoride removal was set by Smith and Davey in their study of the use of bone for defluoridation (18).

CHAPTER 5

RESULTS

This chapter is divided into five major sections. The experimental results for the four systems investigated (virgin bone char, regenerated bone char, virgin activated alumina, and regenerated activated alumina) are presented in the first four sections. The fifth section consists of a general discussion of all the experiments.

For each system, the adsorption isotherm in 10^{-2} M NaCl was first evaluated and then used as an arbitrary standard to facilitate discussions and comparisons. The experimental adsorption data points are presented the first time adsorption isotherm in the 10^{-2} M NaCl is presented; in subsequent isotherm illustrations, the isotherm in 10^{-2} M NaCl is shown as a dashed line.

Virgin Bone Char

Figure 1 shows the effect of sodium chloride ionic strength on the fluoride adsorption isotherms. The greater the ionic strength, the greater the fluoride adsorption. With respect to the 10^{-2} M NaCl isotherm, 10^{-1} M NaCl caused about a 100% increase in removal capacity (X/M) at a 1.0 mg/l F^- equilibrium concentration. The fact that the

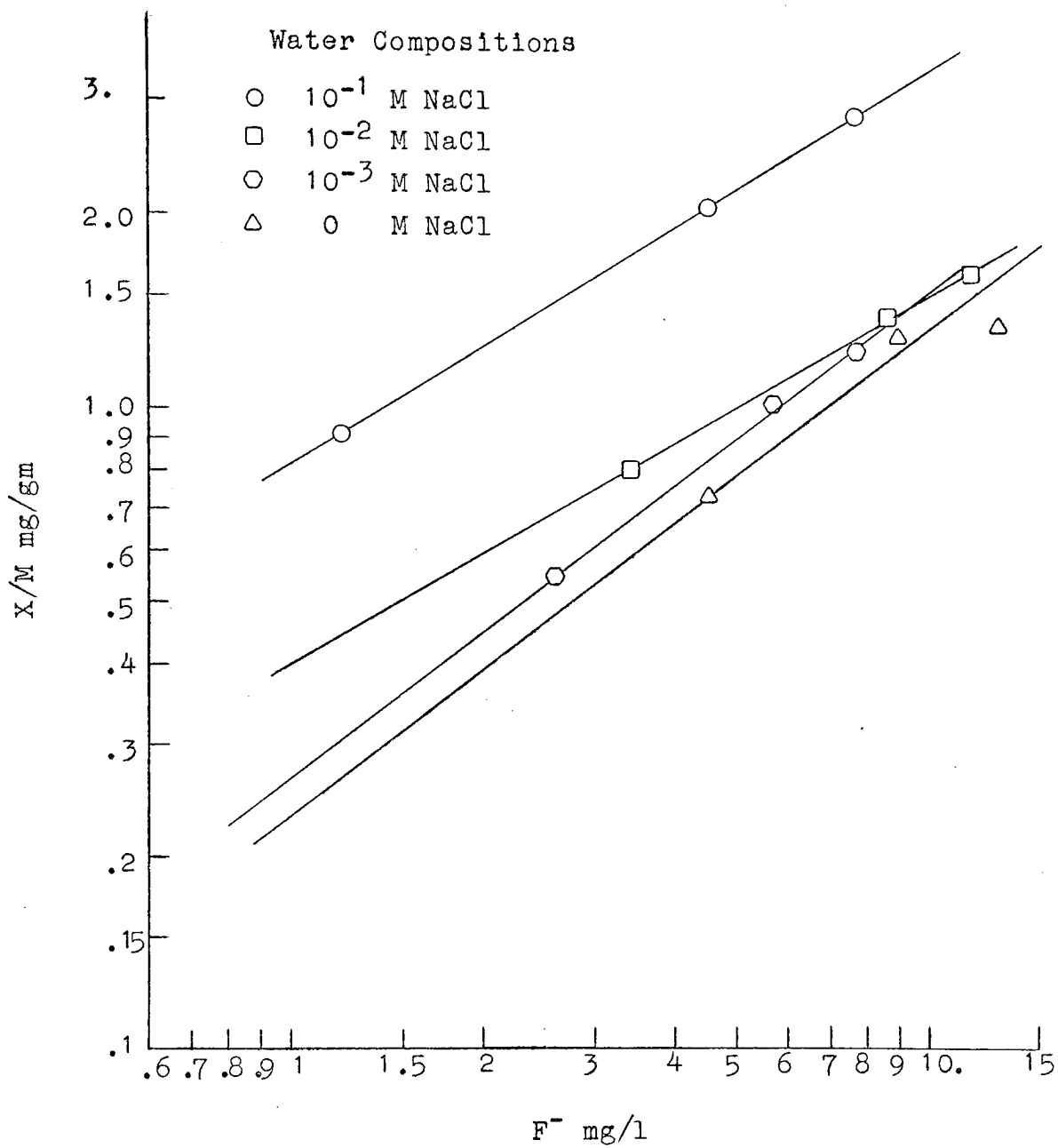


Fig. 1. Effect of Ionic Strength (NaCl) on the Removal of Fluoride by Virgin Bone Char

increased capacity is a function of ionic strength and not Cl^- is shown in Figure 2 where the anions nitrate and chloride are compared. It can also be seen from Figure 2 that there is a small effect of initial pH for the range pH 5.6 to pH 8.8 on the removal capacity. Points at the upper right and at the lower left in Figure 2 suggest that there are three slopes to the isotherm curve over the range of 0.4 to 10 mg/l equilibrium concentration of fluoride.

In Figure 3, the effects of phosphate and bicarbonate on the adsorption isotherm are compared. The dashed line represents the 10^{-2} M NaCl isotherm. The composition of the phosphate system is presented in Table IV.

TABLE IV
SPECIES IN 10^{-2} M PHOSPHATE BUFFER, pH 6.8

Specie	Concentration
H^+	1.6×10^{-7}
K^+	10^{-2} M
H_2PO_4^-	2.8×10^{-3} M
HPO_4^{--}	3.8×10^{-3} M

The system buffered with 10^{-2} M NaHCO_3 shows a reduction of capacity of 38% from the standard system at an equilibrium of 5 mg/l F^- . However, at an equilibrium of 1 mg/l, the capacity is 21% less than that of the

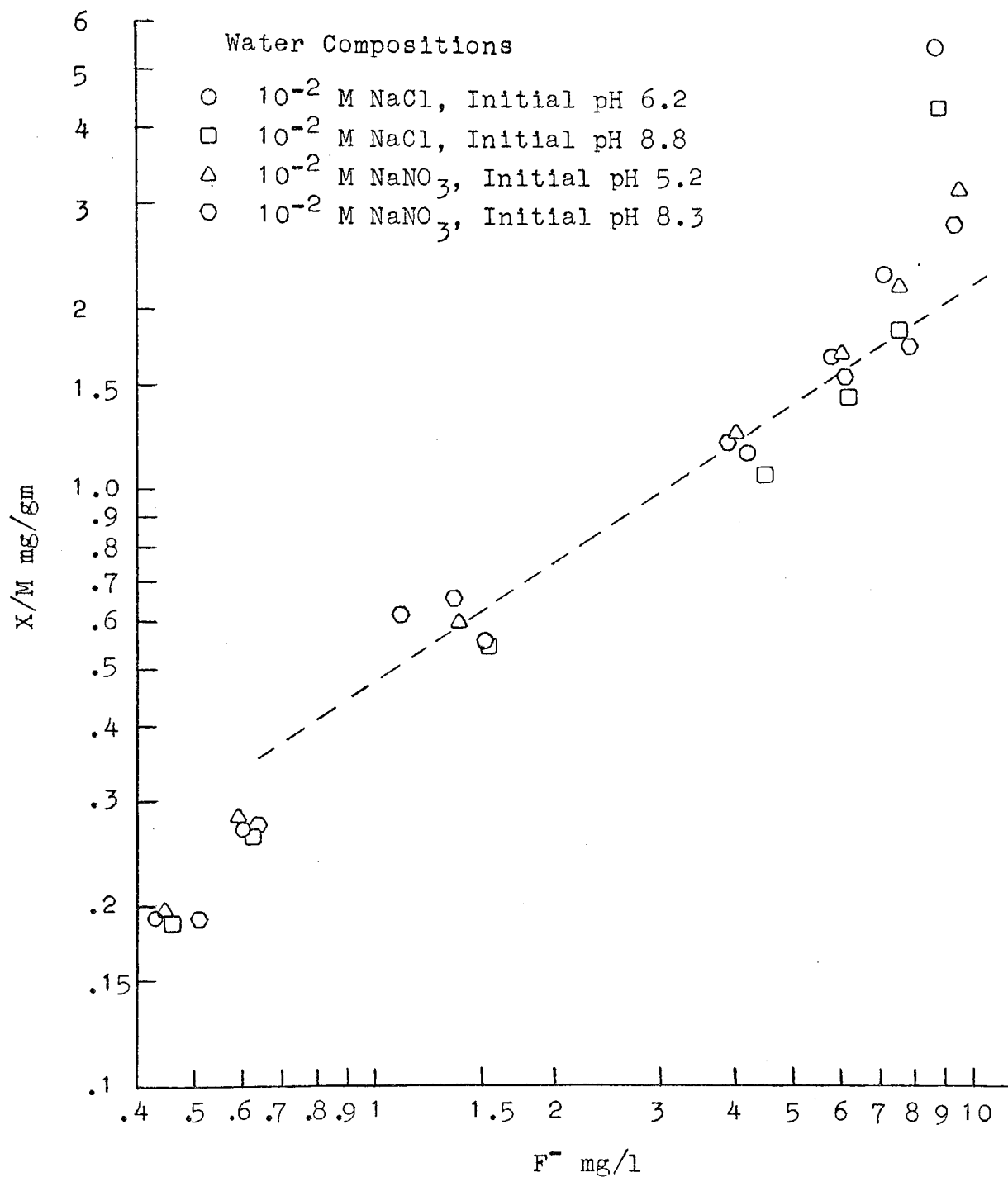


Fig. 2. Effect of Initial Unbuffered pH and Nitrate vs. Chloride on the Removal of Fluoride by Virgin Bone Char

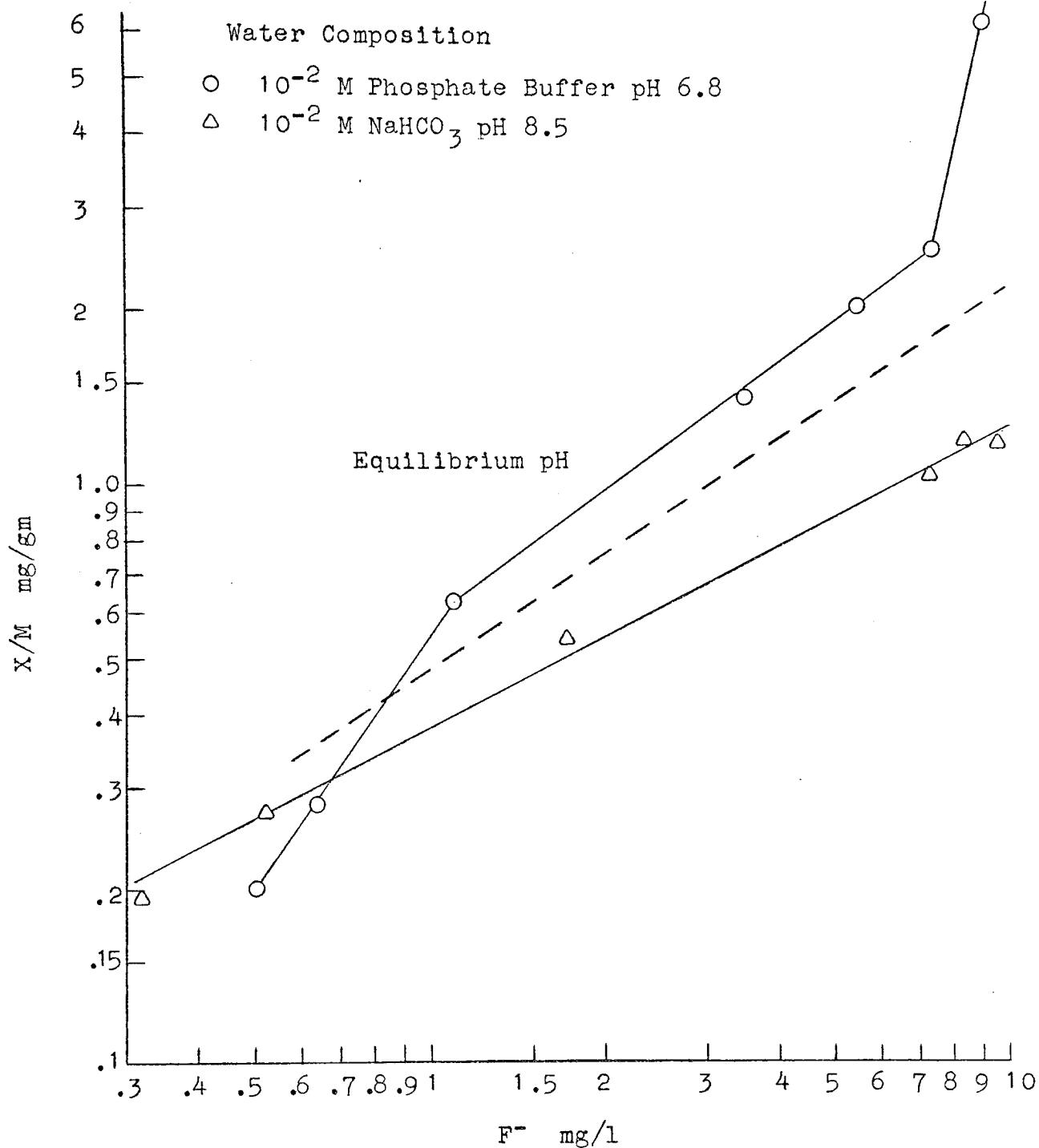


Fig. 3. Effect of Bicarbonate Buffering and Phosphate Buffering on the Removal of Fluoride by Virgin Bone Char

10^{-2} M NaCl curve. Final equilibrium pH values of the systems having residual fluoride concentrations less than 2 mg/l are noted on the plot. The mechanism of ion exchange releasing CO_3^{--} for F^- explains the higher pH at higher fluoride removals (lower fluoride equilibrium concentrations). If the mechanism is indeed one of ion exchange similar to equation 1, the higher pH's at the lower equilibrium concentrations will affect both the bicarbonate buffered and the unbuffered NaCl system essentially the same. The hydroxide released in ion exchange overcomes the buffering capacity of the water. For pH values greater than 9, it is expected that fluoride loadings should decrease with increasing pH's.

Figure 4 shows the effect of different ions. The assumption that the isotherms are straight lines is not quite valid as seen in Figure 2, but the magnitude of the effect is apparent. The Ca^{++} and Mg^{++} ions sharply increase the capacity of the char. At an equilibrium concentration of 1 mg/l fluoride, the capacity is increased 2.5 times with calcium present and 1.6 times with magnesium present when compared to the 10^{-2} M NaCl isotherm. These samples all contained 10^{-4} M phosphate buffer (the buffer described in Table IV diluted 100 fold). The effect of the buffer is negligible compared to the buffering effect of the media itself on the water.

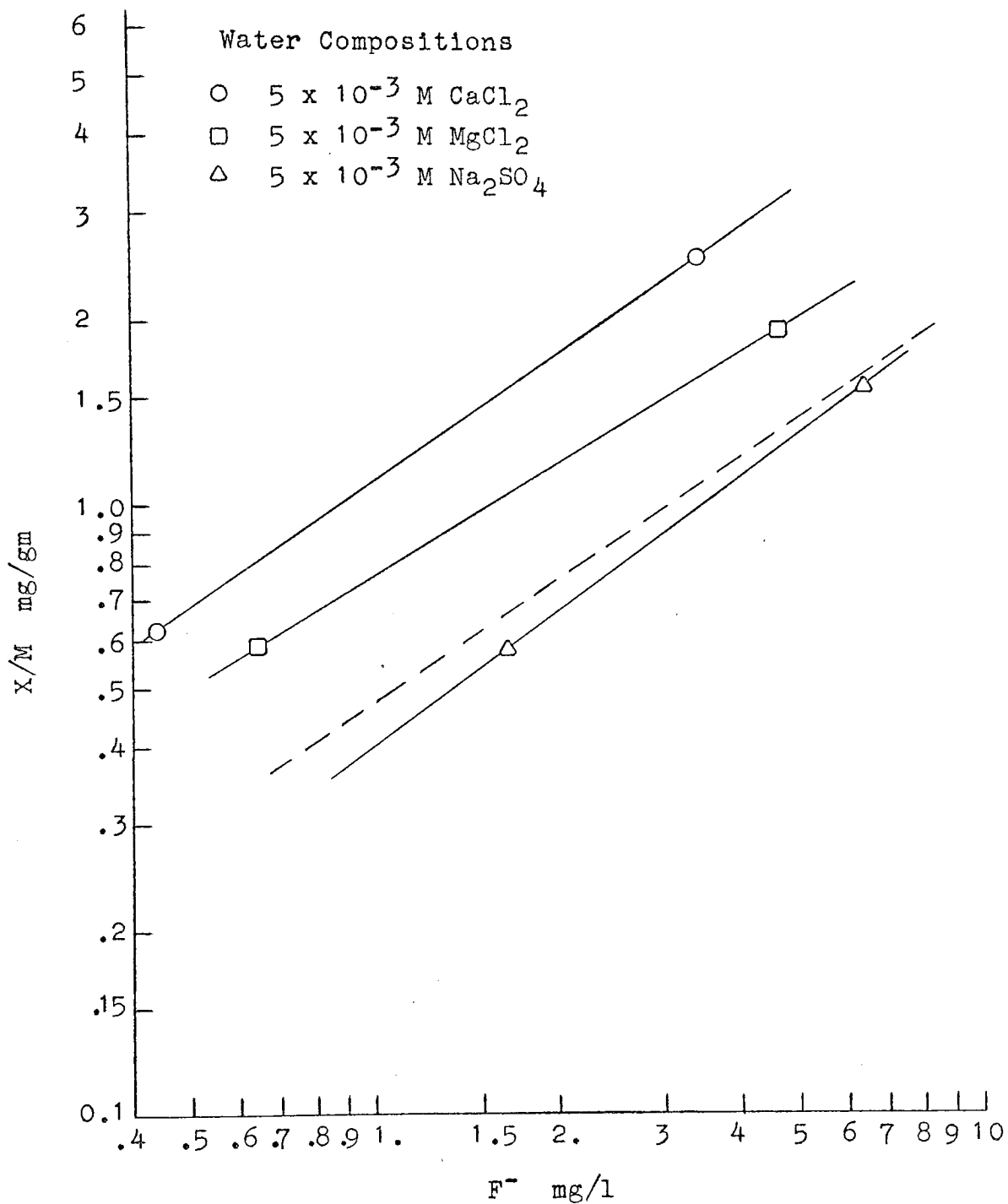


Fig. 4. Effect of 5×10^{-3} M Ca^{++} , 5×10^{-3} M Mg^{++} , and 5×10^{-3} M Na_2SO_4 on Fluoride Removal by Virgin Bone Char

A comparison of the isotherms for the sodium chloride and sodium sulfate systems illustrated in Figure 4 indicate that adsorption is not affected by the presence of the divalent sulfate anion.

Regenerated Bone Char

The results presented in this section are based on experiments conducted with bone char which had been regenerated six times.

The effect of pH on the adsorption capacity is illustrated in Figure 5. The removal of fluoride ions by the media occurs by an ion exchange mechanism in which hydroxide ions are replaced by fluoride ions, equation 3. Hence, the pH increases during the removal reaction. Higher final pH's are associated with lower capacities as seen in Figure 5.

Figure 6 shows the effect of sodium chloride ionic strength on the removal of fluoride. Ionic strength has a definite positive effect on the removal of fluoride and the adsorption capacity of the media. An ionic strength of 10^{-3} M decreased the capacity by 50% compared to an ionic strength of 10^{-2} M while ionic strength of 10^{-1} M increased capacity by 169% at a final fluoride concentration of 1.0 mg/l.

Figure 7 illustrates the effects of CaCl_2 , MgCl_2 , NaCl , and Na_2SO_4 on the fluoride adsorption isotherms.

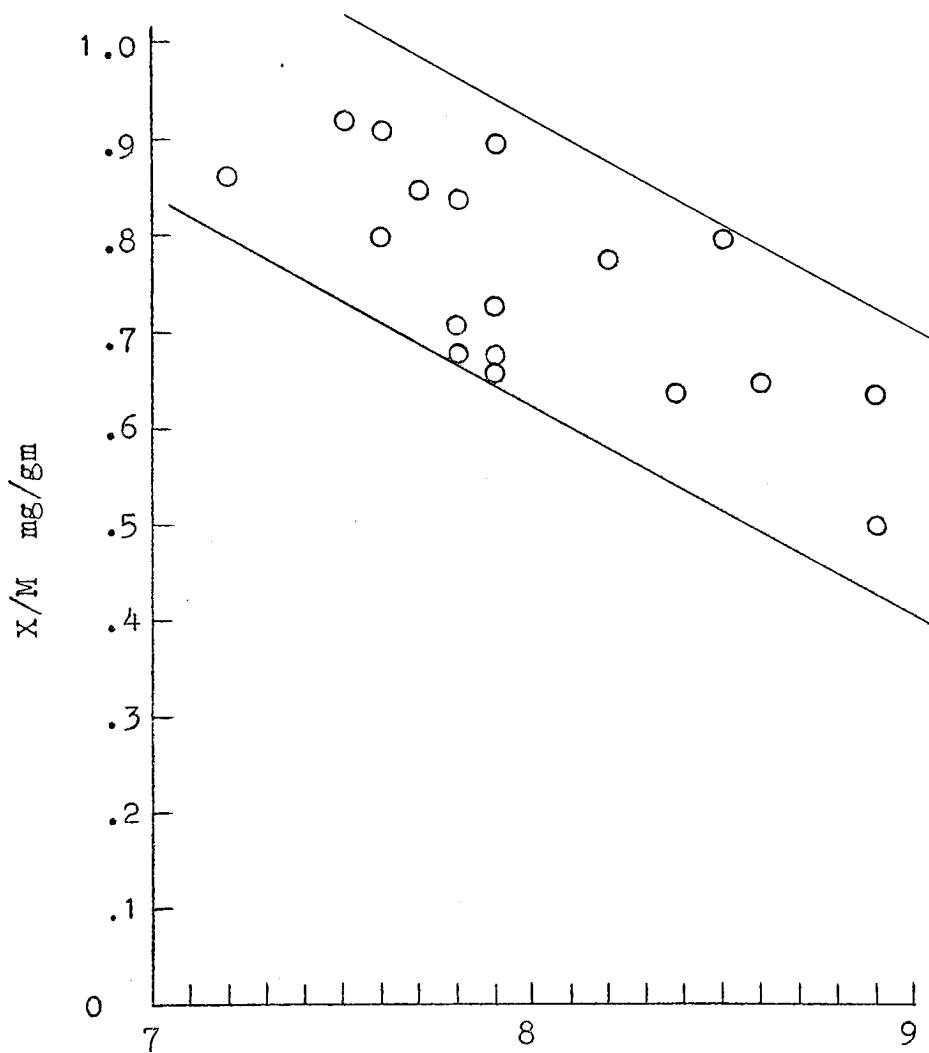


Fig. 5. Effect of Equilibrium pH on Fluoride Loading in Systems with an Initial F^- Concentration of 10 mg/l Ionic Strength equal to 10^{-2} M, and Containing 10 gm/l of Regenerated Bone Char

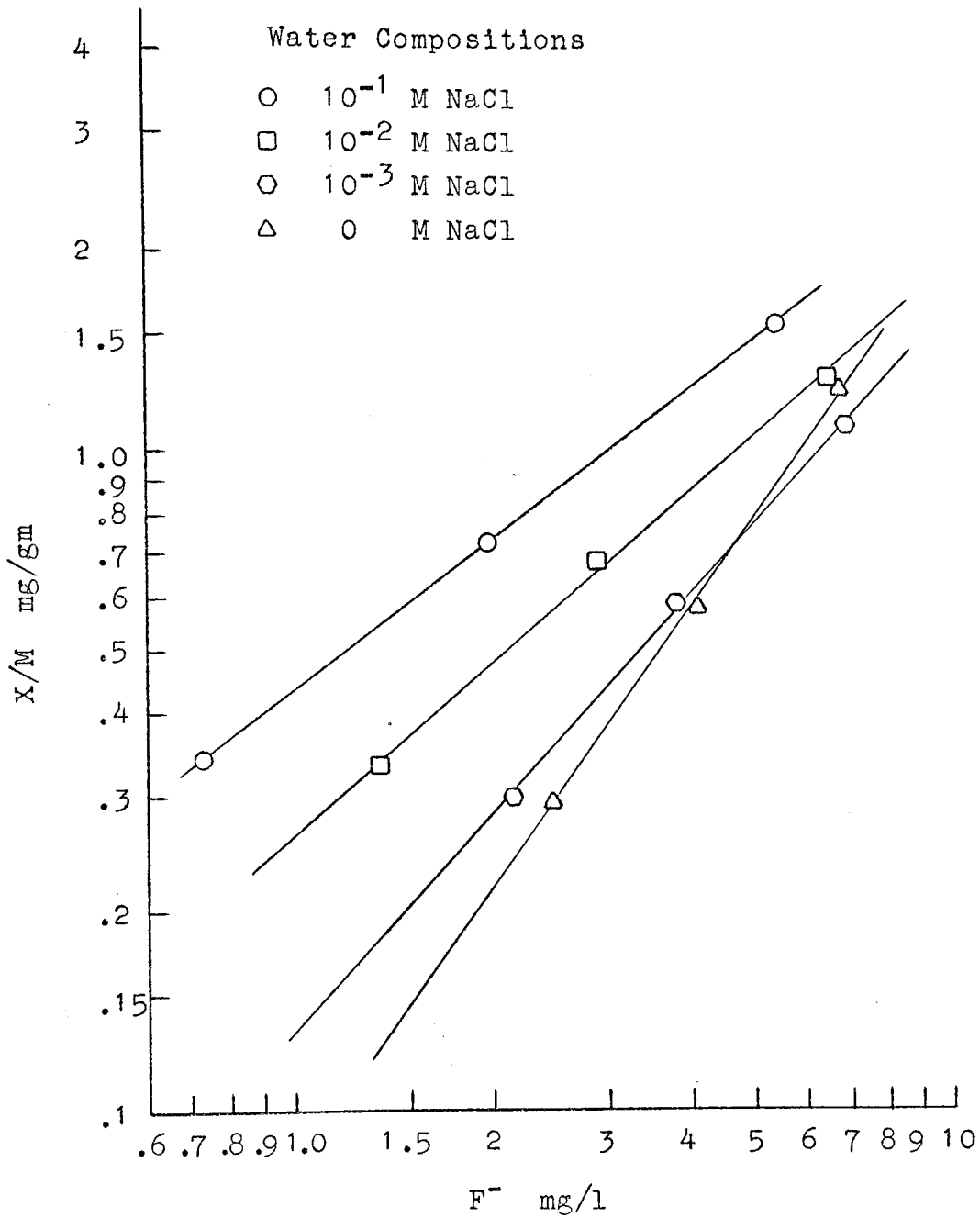


Fig. 6. Effect of Ionic Strength (NaCl) on the Removal of Fluoride by Regenerated Bone Char

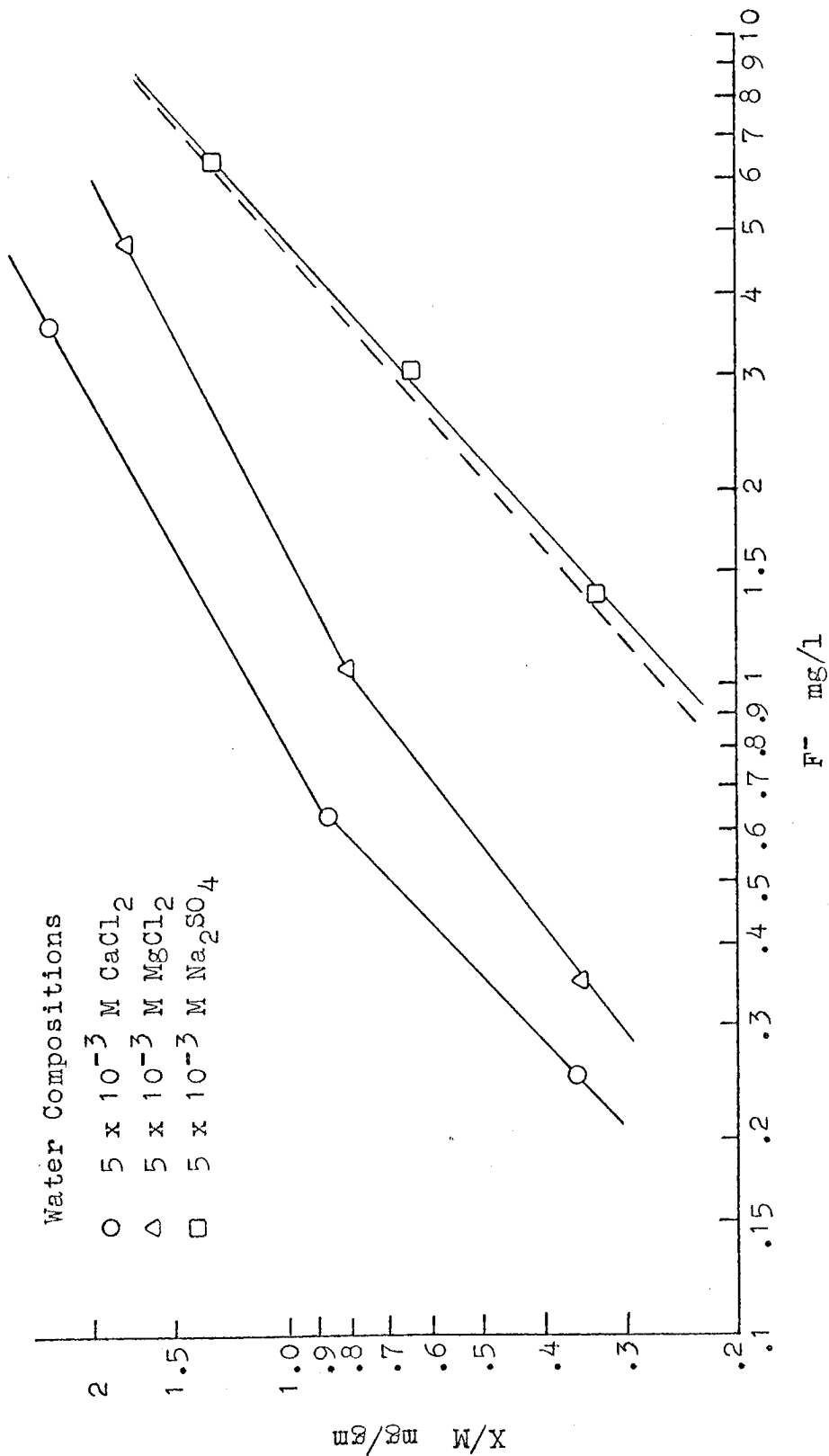


Fig. 7. Effect of 5×10^{-3} M Ca^{++} , 5×10^{-3} M Mg^{++} and 5×10^{-3} M SO_4^{--} on the Removal of Fluoride by Regenerated Bone Char

The chloride ion concentration is equal to 10^{-2} M in the CaCl_2 , MgCl_2 and NaCl systems. The sodium ion concentration is held constant at 10^{-2} M for the NaCl and Na_2SO_4 systems. The data of Figure 7 indicate that divalent cations enhance adsorption in comparison to the monovalent NaCl and Na_2SO_4 systems. Calcium ions seem to cause greater enhancement than magnesium ions. Divalent sulfate ions have a negligible effect on adsorption capacities when compared to systems containing monovalent chloride ions at twice the concentration. Calcium increases the capacity of the media to 4.6 times that of the 10^{-2} M NaCl system at 1 mg/l F^- at equilibrium. Magnesium increases capacity 3.0 times.

The effects of several ions and combinations of ions are shown in Figure 8. Indications are that 10^{-2} M KCl reduces the capacity of the media in the lower regions of the 1 to 10 mg/l equilibrium fluoride range and increases capacity in the upper part. Ten mg/l of arsenic also suppresses the removal in the lower range. The presence of silicate, SiO_2 , suppresses removal by about 40 percent at the 1.0 mg/l F^- equilibrium concentration.

The effect of calcium ion concentrations on fluoride adsorption is shown in Figure 9. The calcium concentrations investigated span the range of values found in approximately 90 percent of the high fluoride waters. The

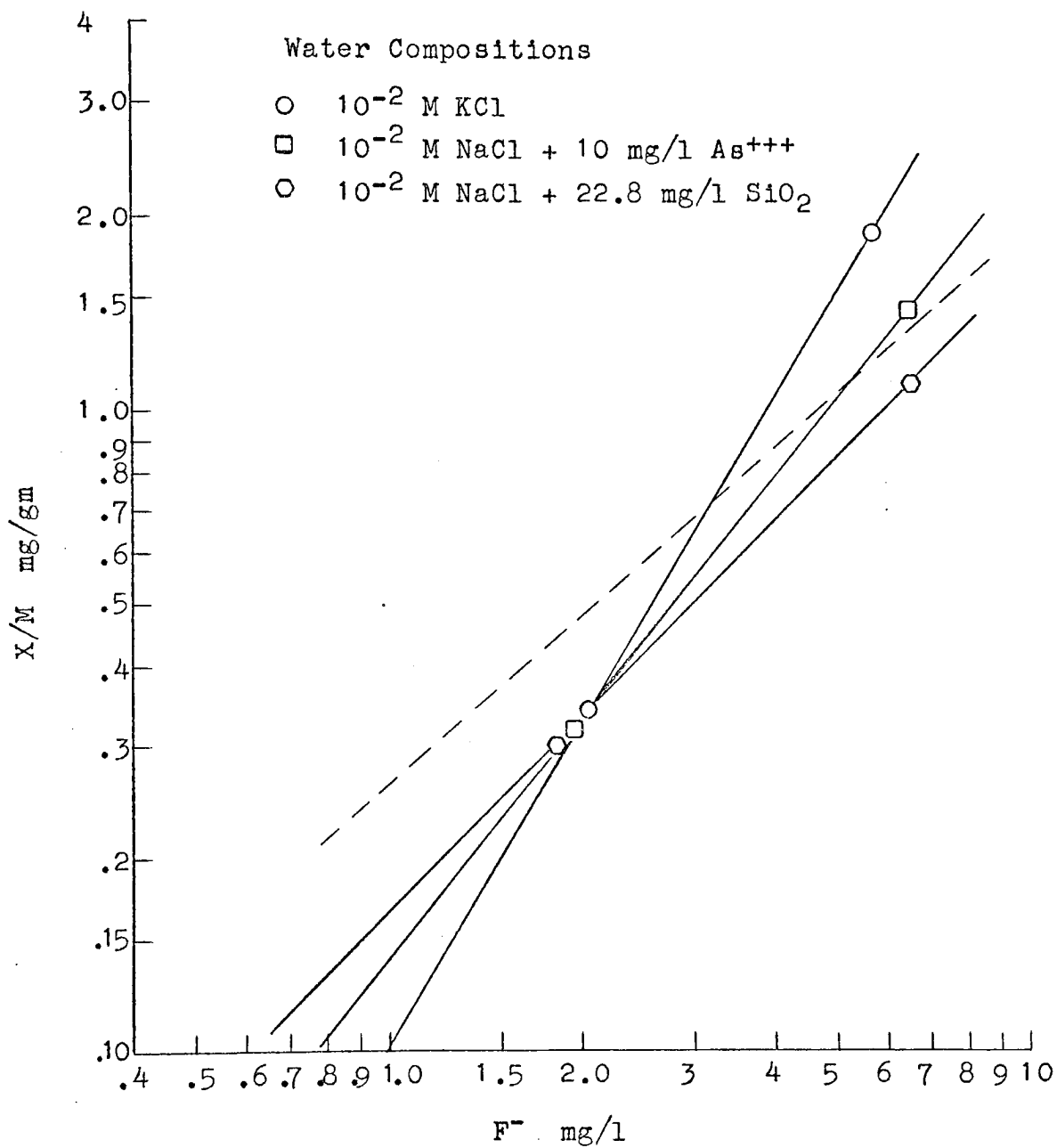


Fig. 8. Effect of 10 mg/l As^{+++} , 10^{-2} M KCl, and 22.8 mg/l SiO_2 on Removal of Fluoride by Regenerated Bone Char

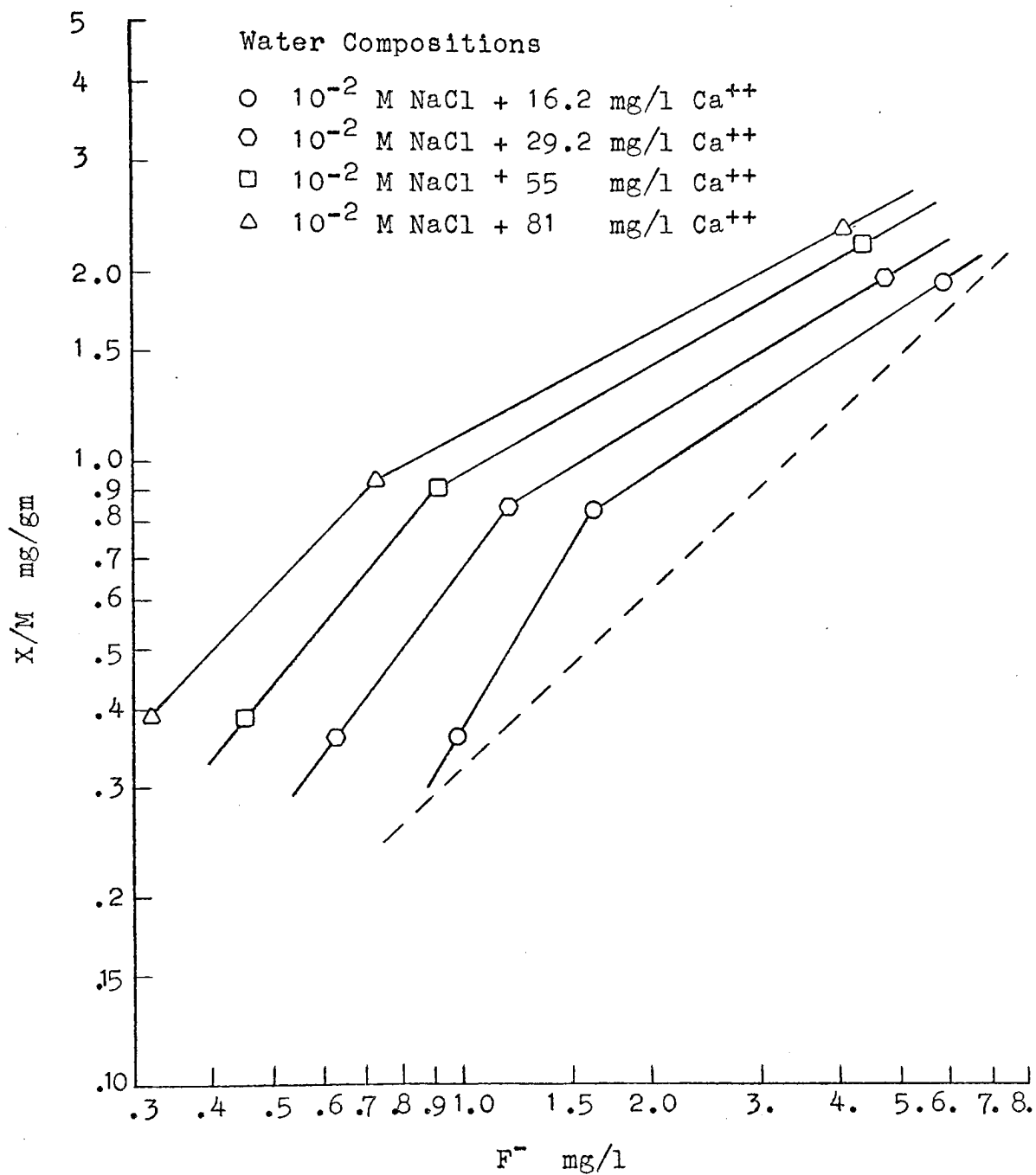


Fig. 9. Effect of Calcium Concentrations on Removal of Fluoride by Regenerated Bone Char

data indicate that adsorption loadings increase with increased calcium concentrations.

Magnesium ions also have a similar effect on adsorption. See Figure 7. The magnesium effect is less important than the effect of calcium because in the majority of Arizona waters with excessive fluorides the calcium concentrations are much greater than the magnesium concentrations. Hence, no additional investigations on the magnesium system were conducted.

The effects of various concentrations of bicarbonate are shown in Figure 10. The values used were based on the statistical typical water composition data from the computer study. Constant ionic strength was maintained by the addition of NaCl. There is a definite reduction of the capacity of 0.5 gms of media reacting with 200 ml of 10 mg/l F^- water.

An experiment was performed to determine if the reduction of capacity was due to the bicarbonate ion or the high pH. The isotherm for a 10^{-2} M bicarbonate solution and a 10^{-2} M phosphate solution pH 7.7 are shown in Figure 11. The species distribution of the phosphate buffer is shown in Table V. Even though the starting pH values of these buffered systems were different, the reduction of the capacity is the same at an equilibrium fluoride concentration of 2.5 mg/l. Also, in Figure 11, the isotherm for 10^{-2} M NaCl plus 10^{-4} M phosphate buffer

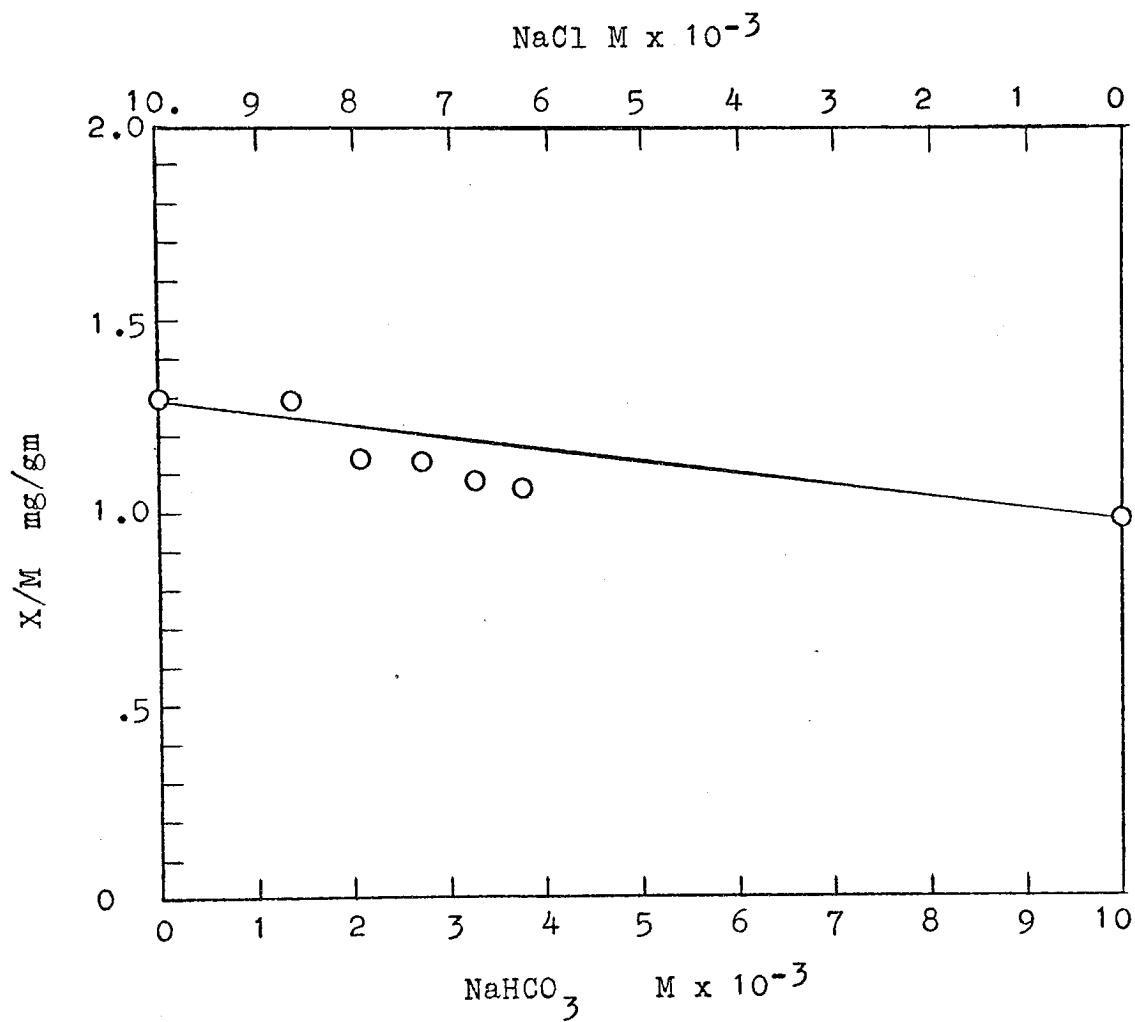


Fig. 10. Effect of Bicarbonate Concentration on Fluoride Sorption by Bone Char at Constant Mass of Media per Unit Volume (1.5 gm/l), Constant Ionic Strength, and from 10 mg/l Fluoride

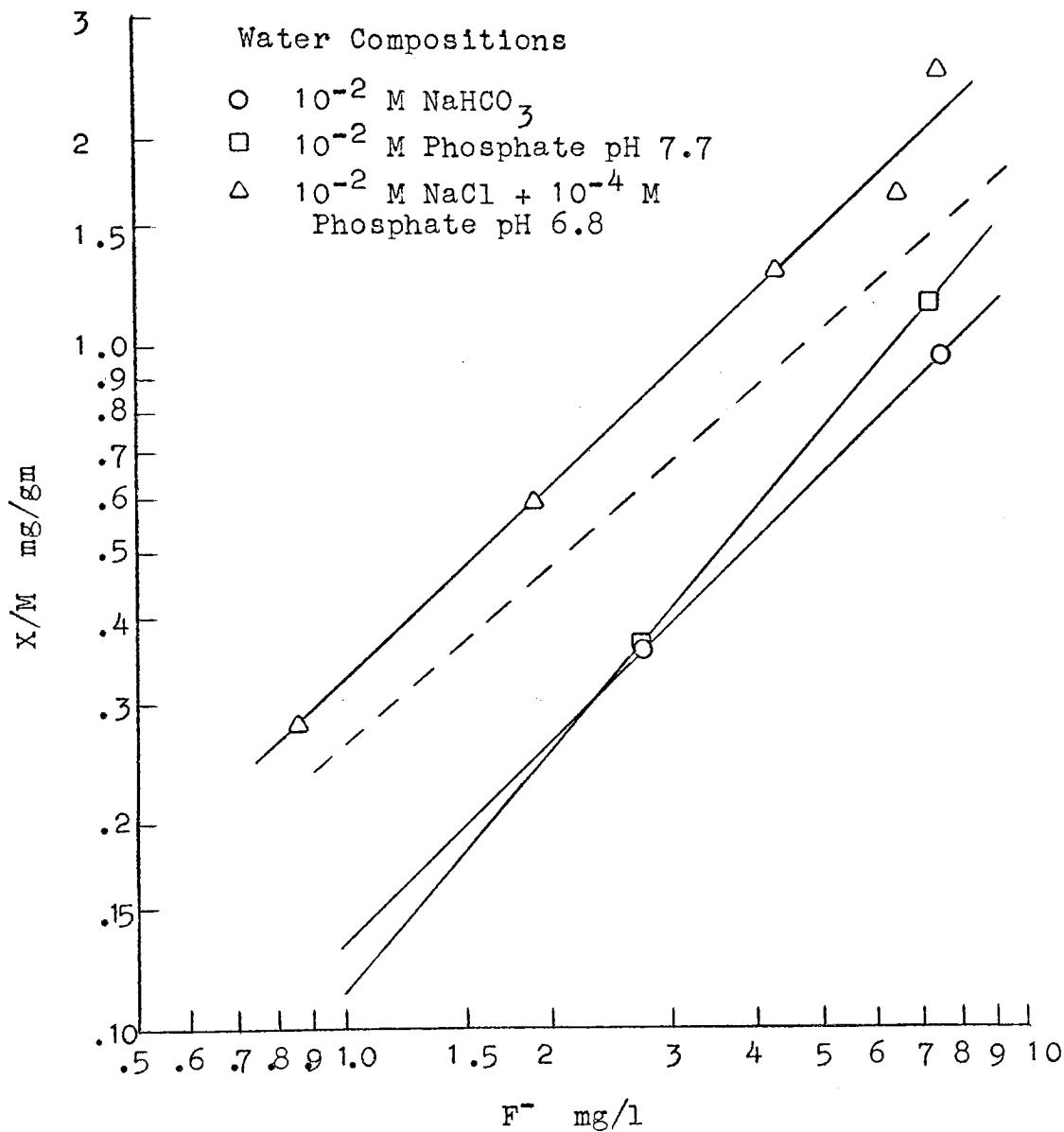


Fig. 11. Effect of 10^{-2} M Bicarbonate and 10^{-2} M Phosphate Buffer, pH 7.7, on Fluoride Removal by Regenerated Bone Char

at pH 6.8 is shown. The small amount of buffer increases the capacity by 23% at the 2.0 mg/l equilibrium concentration.

TABLE V
SPECIES IN 10^{-2} M PHOSPHATE BUFFER, pH 7.7

Specie	Concentration
H^+	2.0×10^{-8} M
K^+	1.54×10^{-2} M
HPO_4^{--}	$.72 \times 10^{-2}$ M
$H_2PO_4^-$	$.10 \times 10^{-2}$ M

The comparative efficiencies of removal for three waters containing calcium ions is demonstrated in Figure 12. A water with 29.2 mg/l calcium plus 166 mg/l bicarbonate shows an increase in removal capacity of 69% over the 10^{-2} M NaCl isotherm at a fluoride equilibrium of 1.0 mg/l. A synthetic water, Table VI, increased removal by 85%. A water with 29.2 mg/l calcium increased removal by 180%. It is apparent that the positive effect of the calcium concentration was great enough to overcome the negative effect of the bicarbonate concentration and effect an overall increase in removal of fluoride compared to the 10^{-2} M NaCl curve. The calcium, while dominant is not the only factor in a calcium-bicarbonate system since the

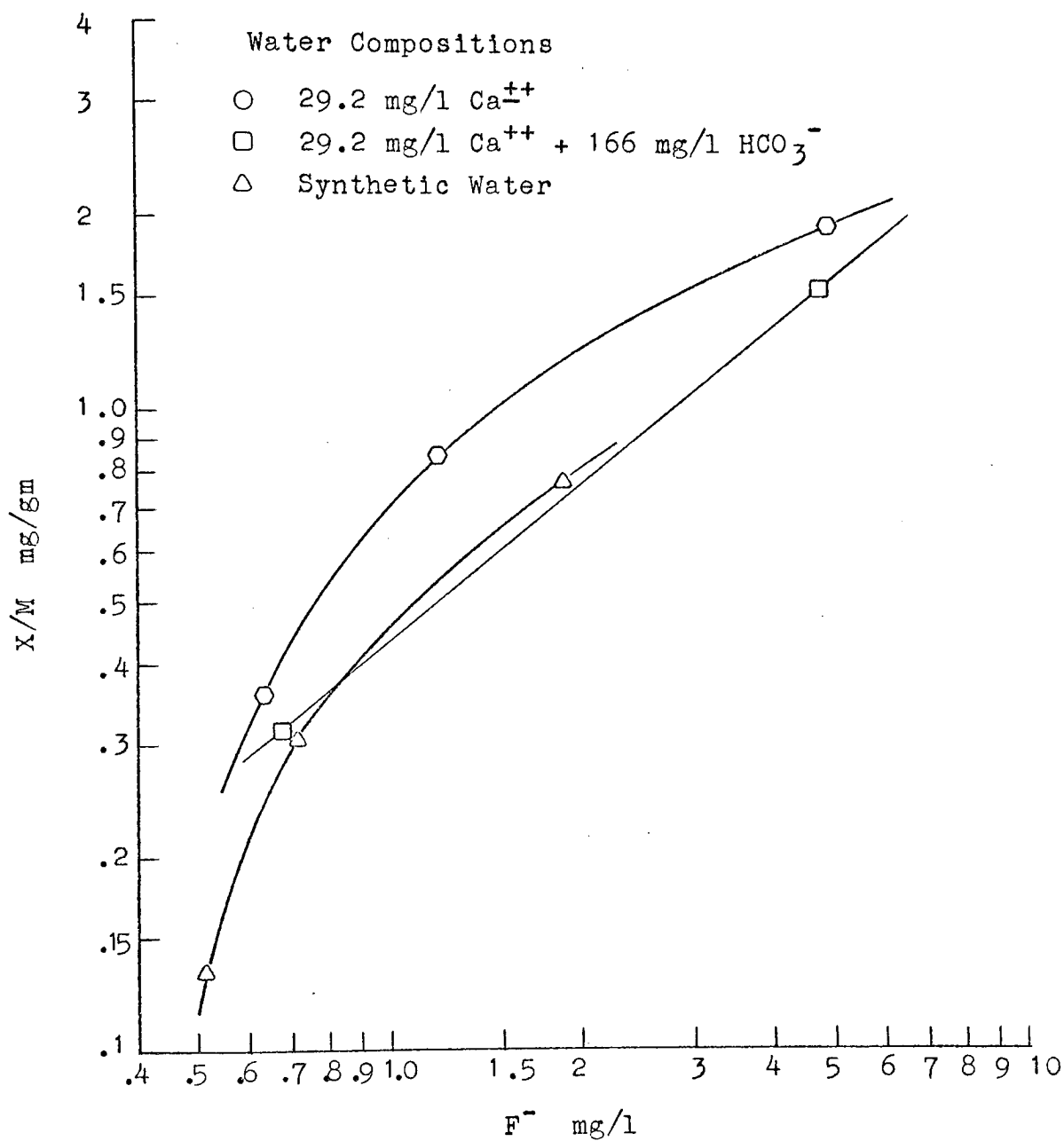


Fig. 12. Comparative Effects of Three Calcium Containing Waters on the Removal of Fluoride by Regenerated Bone Char

capacity of the media is not as great in a calcium bicarbonate system as it is in a calcium system.

TABLE VI
SYNTHETIC WATER COMPOSITION

Component	Concentration mg/l
Calcium	29.2
Magnesium	9.1
Potassium	15.2
Sodium	121
Bicarbonate	166
Chloride	86.5
Fluoride	4.1
Nitrate	4.2
Sulfate	111

The fact that the reaction removing fluoride is believed to be one of ion-exchange for hydroxyl, and the fact that the media showed a tendency to raise the pH of solutions containing no fluoride led to an experiment to separate the phenomena. Two 200 ml samples, each 10^{-2} M NaCl, one with 9.1 mg/l F^{-} , Sample A, and the other with no fluoride, Sample B, were treated with two grams of bone char. The resulting pH of Sample A was 8.4. Upon titration, it was found that 50 ml of Sample A contained

1.0×10^{-4} equivalents/l of alkalinity to pH 7.0. Sample B at equilibrium was at pH 8. It required 1.5×10^{-4} equivalents of acid to titrate to pH 7.0. The difference in these two values should be the amount contributed by the ion-exchange for fluoride. With an initial concentration of 9.1 mg/l and a final concentration of 4.2 mg/l, 4.9 mg/l or 2.6×10^{-4} moles of fluoride was removed.

All the data indicate that the removal reaction is very complex, with such influencing factors as the buffering capacity of the water, the buffering added by the media, and any auxiliary reactions such as CaF_2 precipitation.

Virgin Activated Alumina

The effects of ionic strength on the uptake of fluoride by activated alumina are shown in Figure 13. One fact stands out clearly. An ionic strength of 10^{-1} M increased removal to 148% of that of the 10^{-3} M ionic strength solution at an equilibrium concentration of 2 mg/l fluoride. The points on the curves for 10^{-2} M, 10^{-3} M, and 0 M ionic strength are clustered enough to suggest that there is no essential difference in the curves presented. The 10^{-2} M NaCl curve will be carried forward without data points to other figures as a basis for comparison.

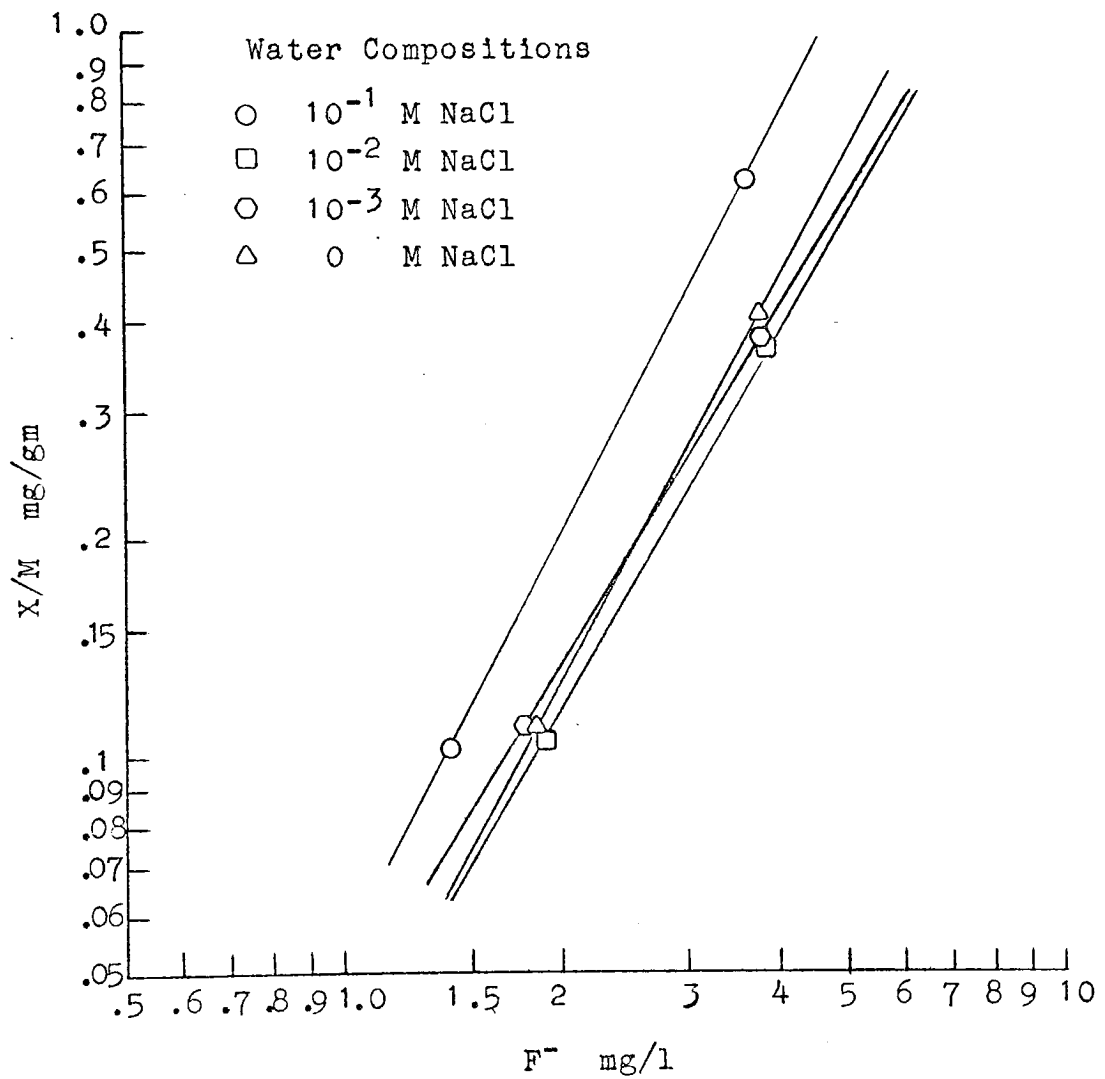


Fig. 13. Effect of Ionic Strength (NaCl) on Fluoride Removal By Virgin Activated Alumina

The data illustrated in Figure 14 demonstrate two things. First, nitrate and chloride behave similarly as background ions. Second, there is little difference caused by unbuffered starting pH. Representative final pH's are shown on the plot.

Effects of calcium, magnesium, and sulfate are presented in Figure 15. The sulfate isotherm falls close enough to the 10^{-2} NaCl isotherm to suggest that there is negligible effect from the divalent sulfate anion. The sorption capacity is greatly enhanced by the presence of magnesium and calcium ions. At an equilibrium level of 2 mg/l F^- the capacity of the media for fluoride in a water containing either 5×10^{-3} M Ca^{++} or 5×10^{-3} M Mg^{++} is 10 times that for a water containing 10^{-2} M Na^+ .

Regenerated Activated Alumina

The effect of equilibrium pH on the capacity of the regenerated activated alumina is illustrated in Figure 16. It is evident that the higher final pH's are associated with lower capacities (X/M). The pH dependence agrees with the ion exchange reaction by which hydroxyl is replaced by fluoride as described in equation 4.

Figure 17 illustrates the effect of sodium chloride ionic strength on the sorption of fluoride by regenerated activated alumina. The important result is the higher the ionic strengths (NaCl) cause lower the removal capacities.

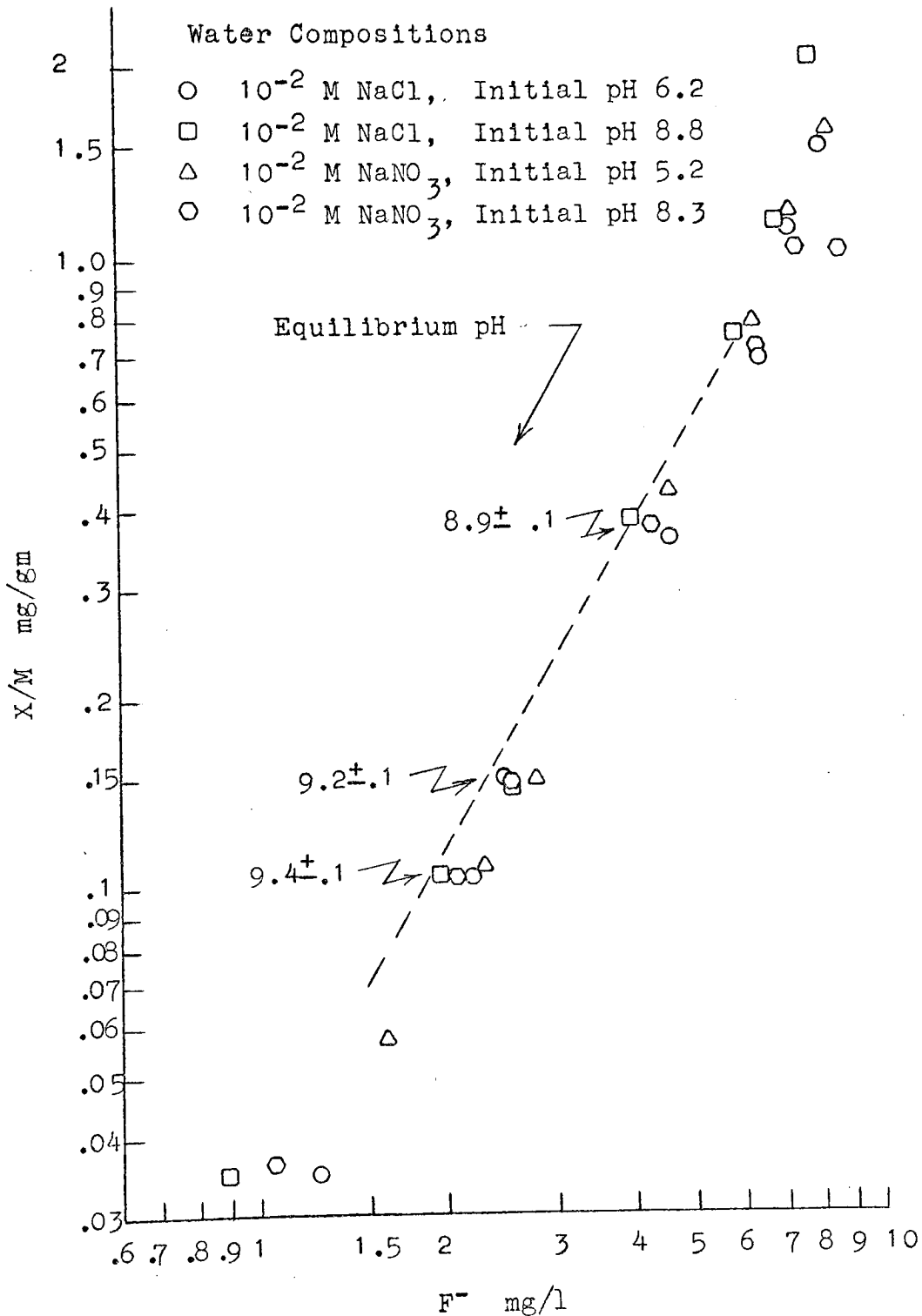


Fig. 14. Effect of Nitrate, Chloride, and Unbuffered Initial pH on Fluoride Removal by Virgin Activated Alumina

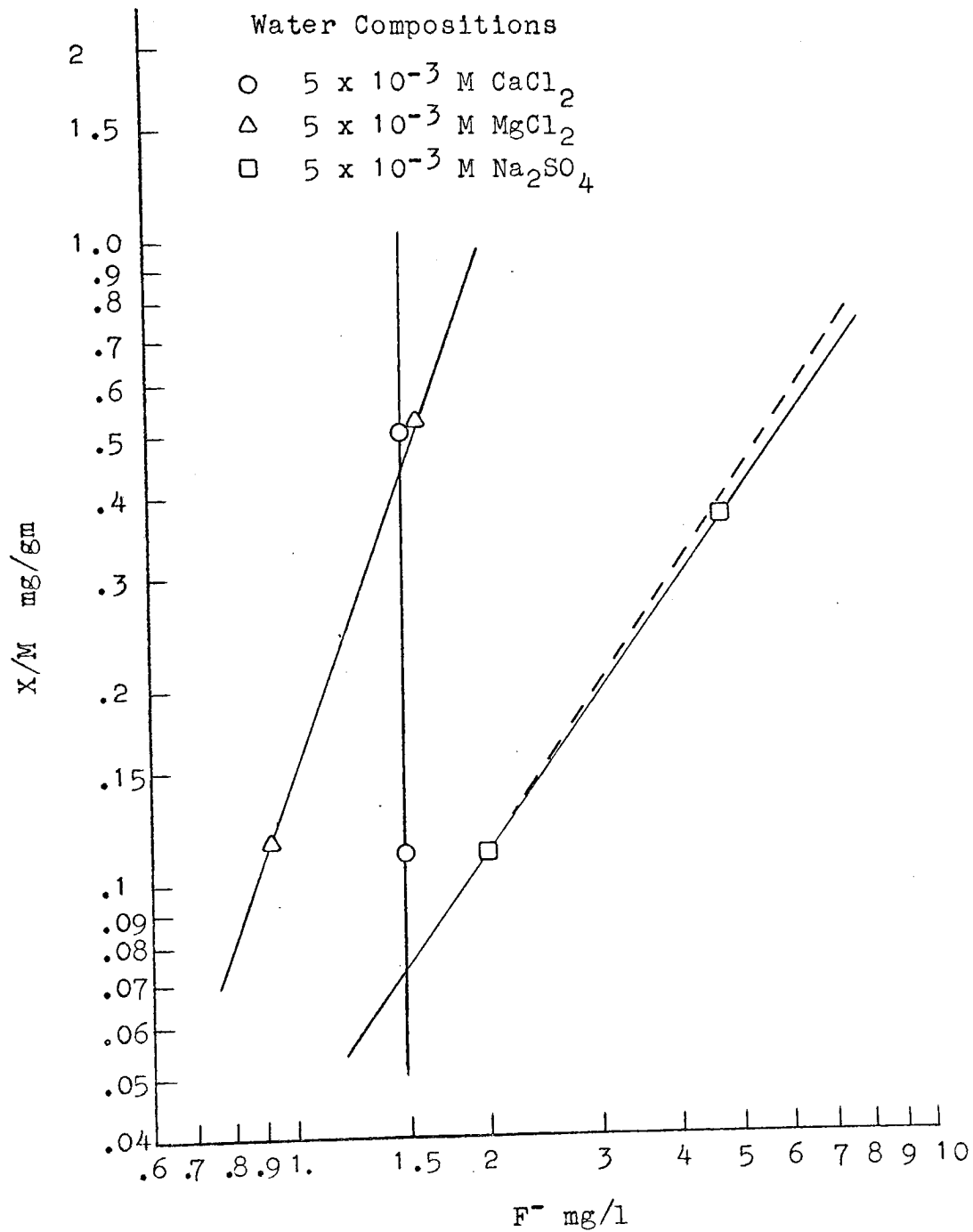


Fig. 15. Effect of 5×10^{-3} M Ca^{++} , 5×10^{-3} M Mg^{++} , and 5×10^{-3} M SO_4^{--} on Fluoride Removal by Virgin Activated Alumina

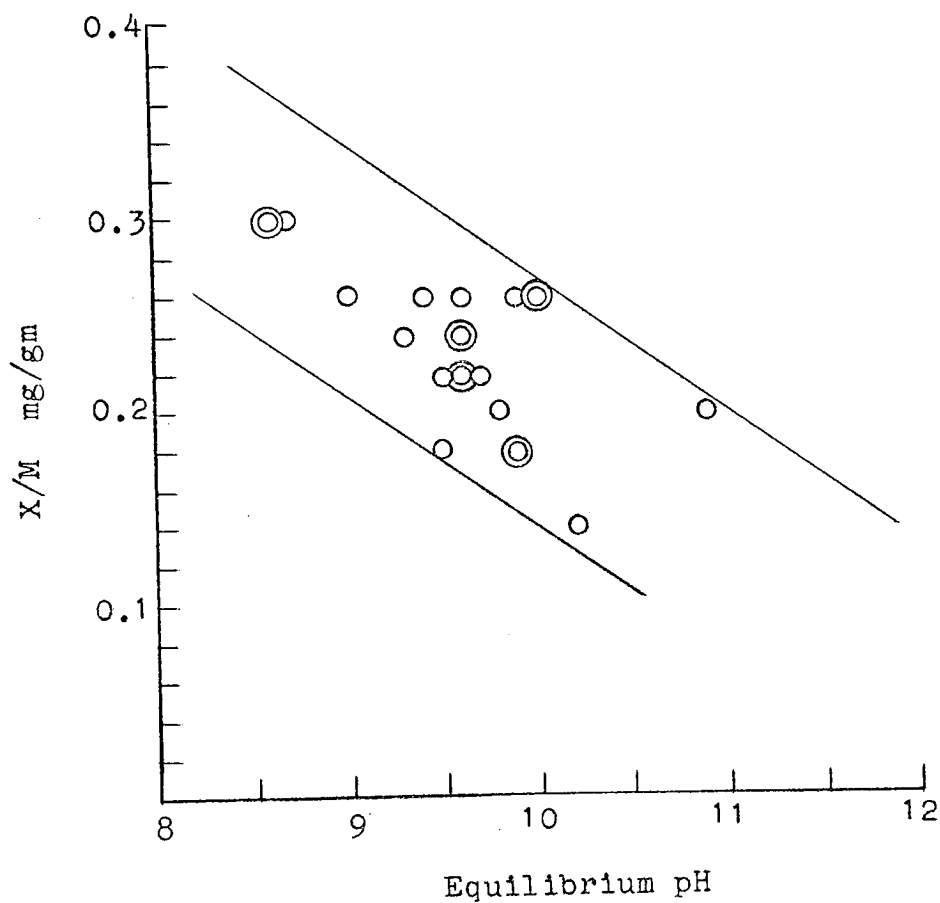


Fig. 16. Effect of Equilibrium pH on Fluoride Loading in Systems with an Initial F^- Concentration of 10 mg/l, Ionic Strength equal to 10^{-2} M, and Containing 25 gm/l of Regenerated Activated Alumina

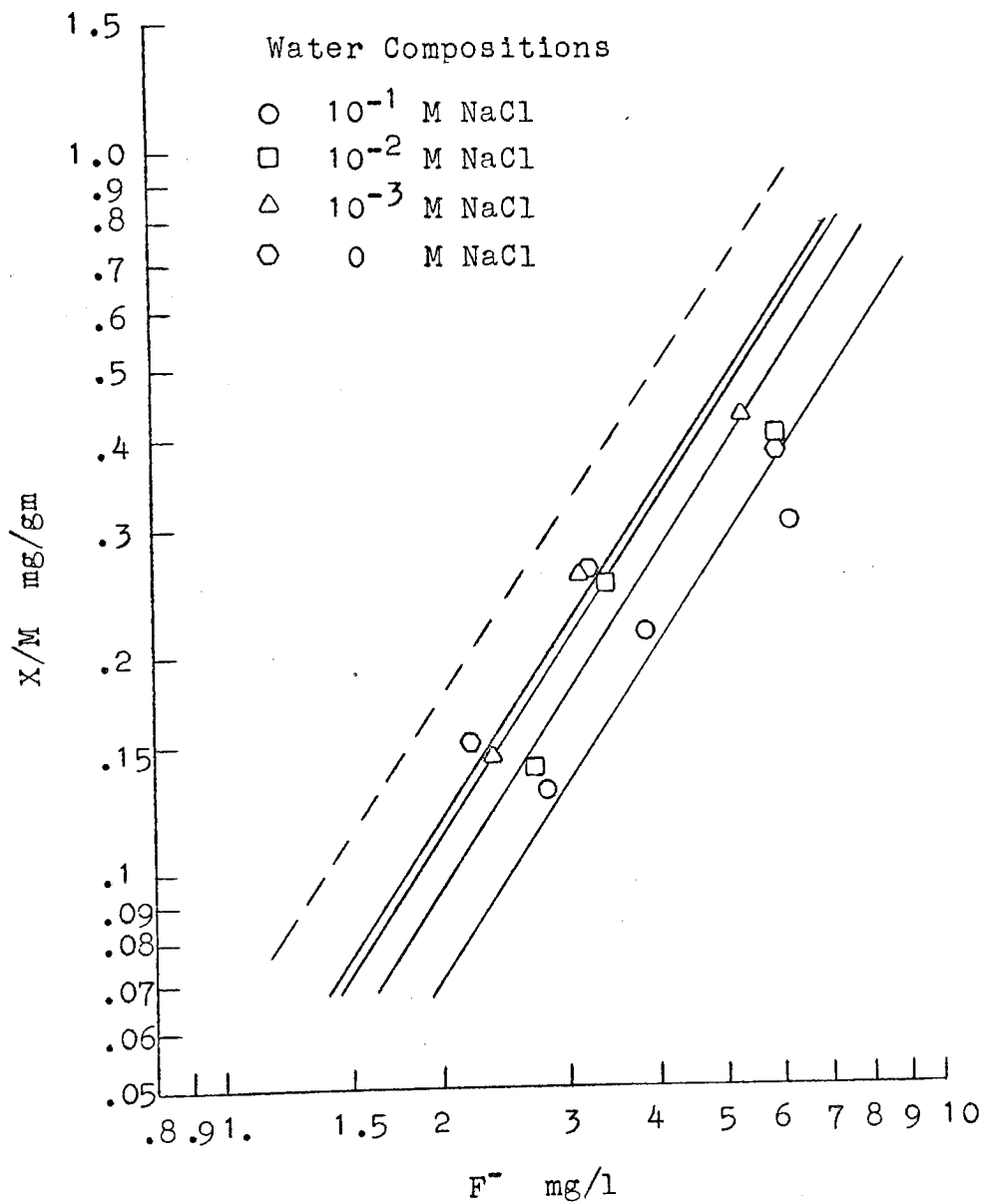


Fig. 17. Effect of Ionic Strength (NaCl) on Removal of Fluoride by Regenerated Activated Alumina

Three isotherms are shown in Figure 18. An isotherm for 10^{-2} M NaCl + 10^{-4} M phosphate buffer and an extension of the 10^{-2} M NaCl curve are compared to the 10^{-2} M NaCl curve. The three points for the extension of the 10^{-2} M NaCl isotherm are seen to fall into the trend established by the 10^{-2} M NaCl curve. The phosphate buffered curve indicates that the 10^{-4} M phosphate buffer is sufficient to raise the removal capacity of the media in sodium chloride systems. It is not possible to determine if the effect was due to pH or phosphate.

The effects of sodium calcium, magnesium, chloride, and sulfate ions on the sorption isotherms are compared in Figure 19. The solutions concentrations were chosen so that the concentration of the ion common in the systems being compared was held constant, i.e., Cl^- equal to 10^{-2} M in the CaCl_2 , MgCl_2 and NaCl systems.

It can be seen that the sorption capacity in those systems containing Mg^{++} and Ca^{++} is greater than the capacity of the Na^+ system. Also, the replacement of $\text{SO}_4^{=}$ for Cl^- increases sorption capacity in the higher equilibrium ranges. Na^+ concentration is constant in the NaCl and Na_2SO_4 systems.

The effects of four concentrations of calcium based on the computer study results are shown in Figure 20. At low equilibrium concentrations of fluoride calcium reduced adsorption and the effect of varying concentrations of Ca^{++}

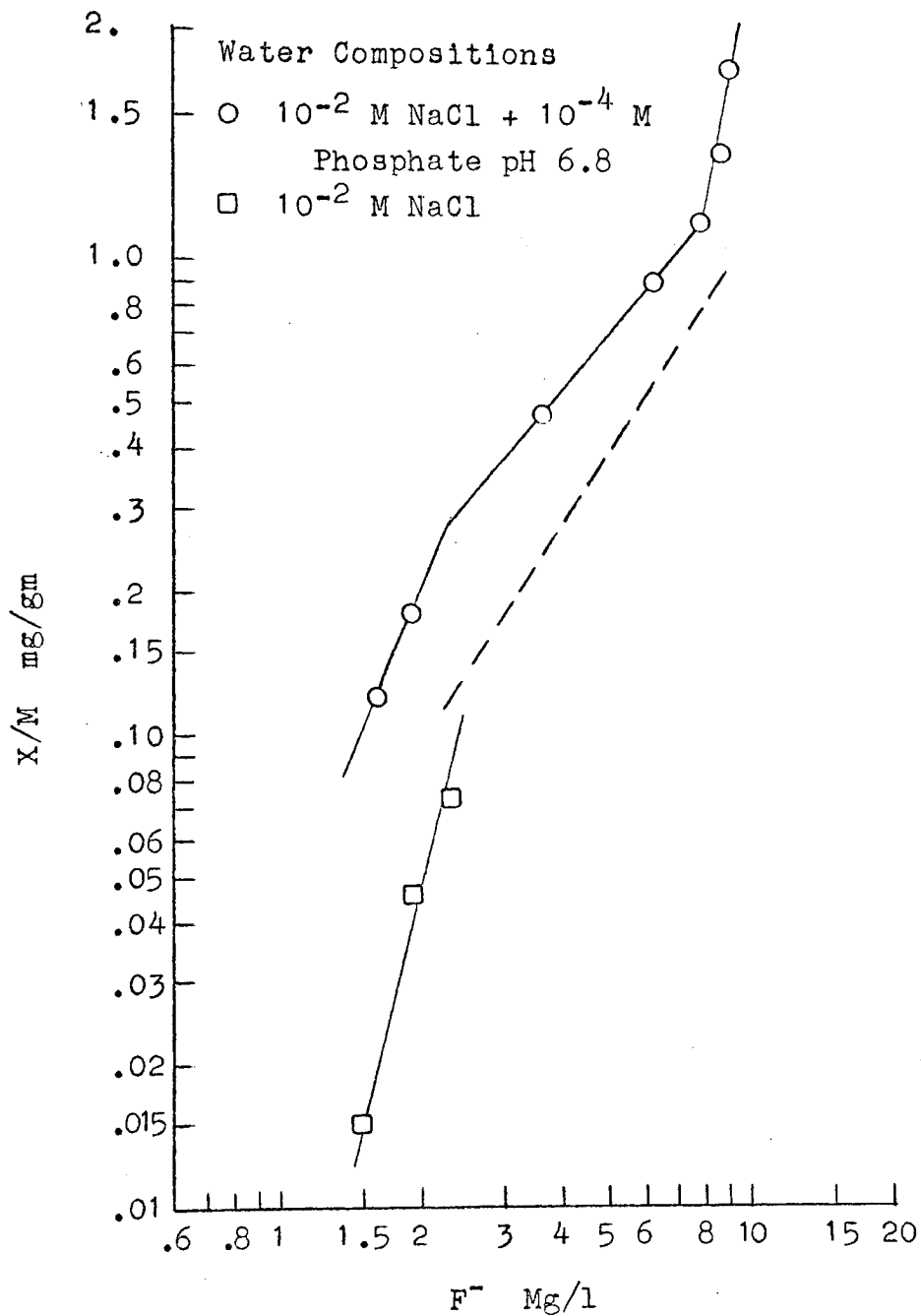


Fig. 18. An Extension of the 10^{-2} M NaCl Isotherm and the Effect of a 10^{-4} M Phosphate Buffer, pH 6.8, on Fluoride Removal by Regenerated Activated Alumina

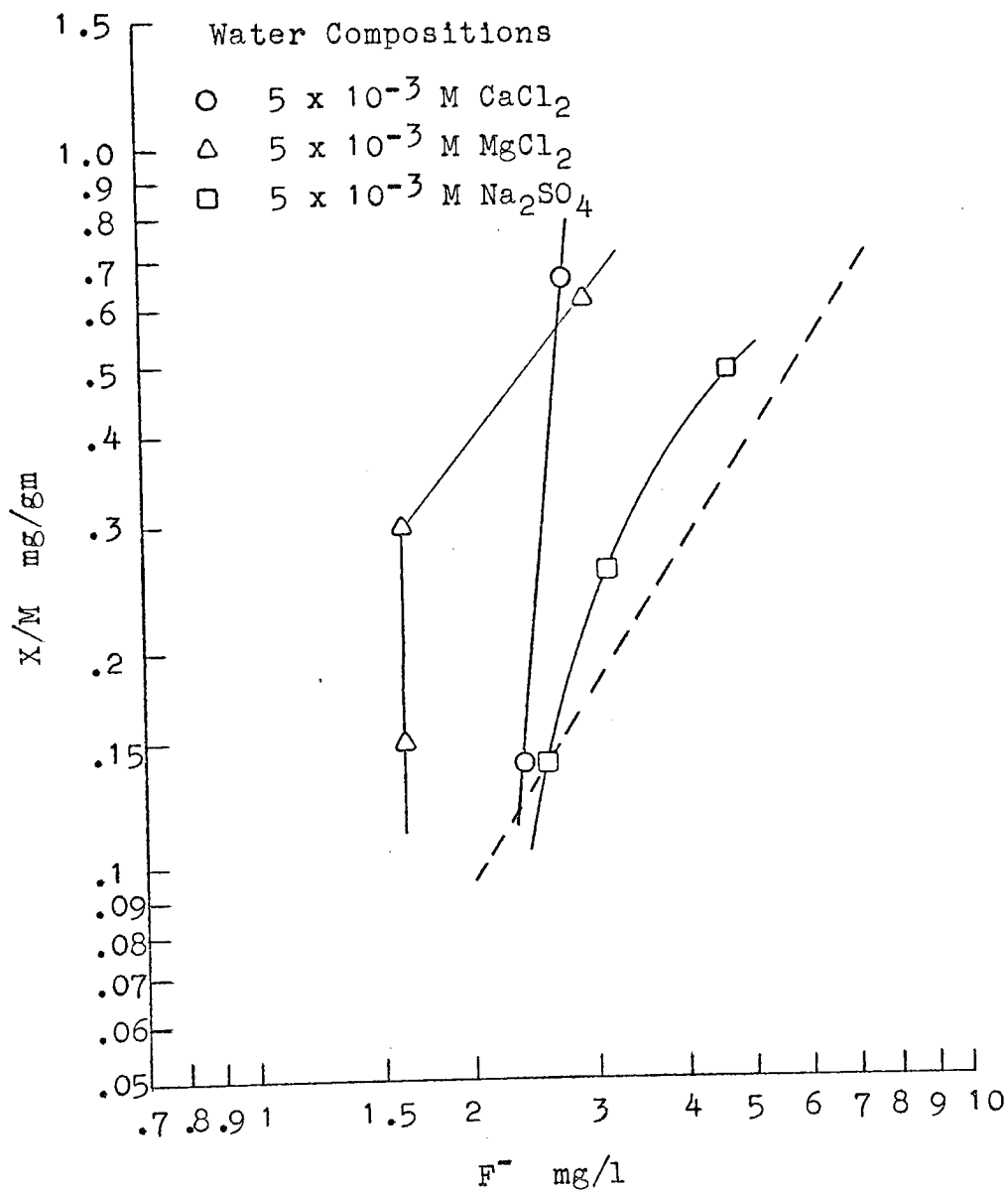


Fig. 19. Effect of 5×10^{-3} M Ca^{++} , 5×10^{-3} M Mg^{++} , and 5×10^{-3} M SO_4^{--} on Fluoride Removal by Regenerated Activated Alumina

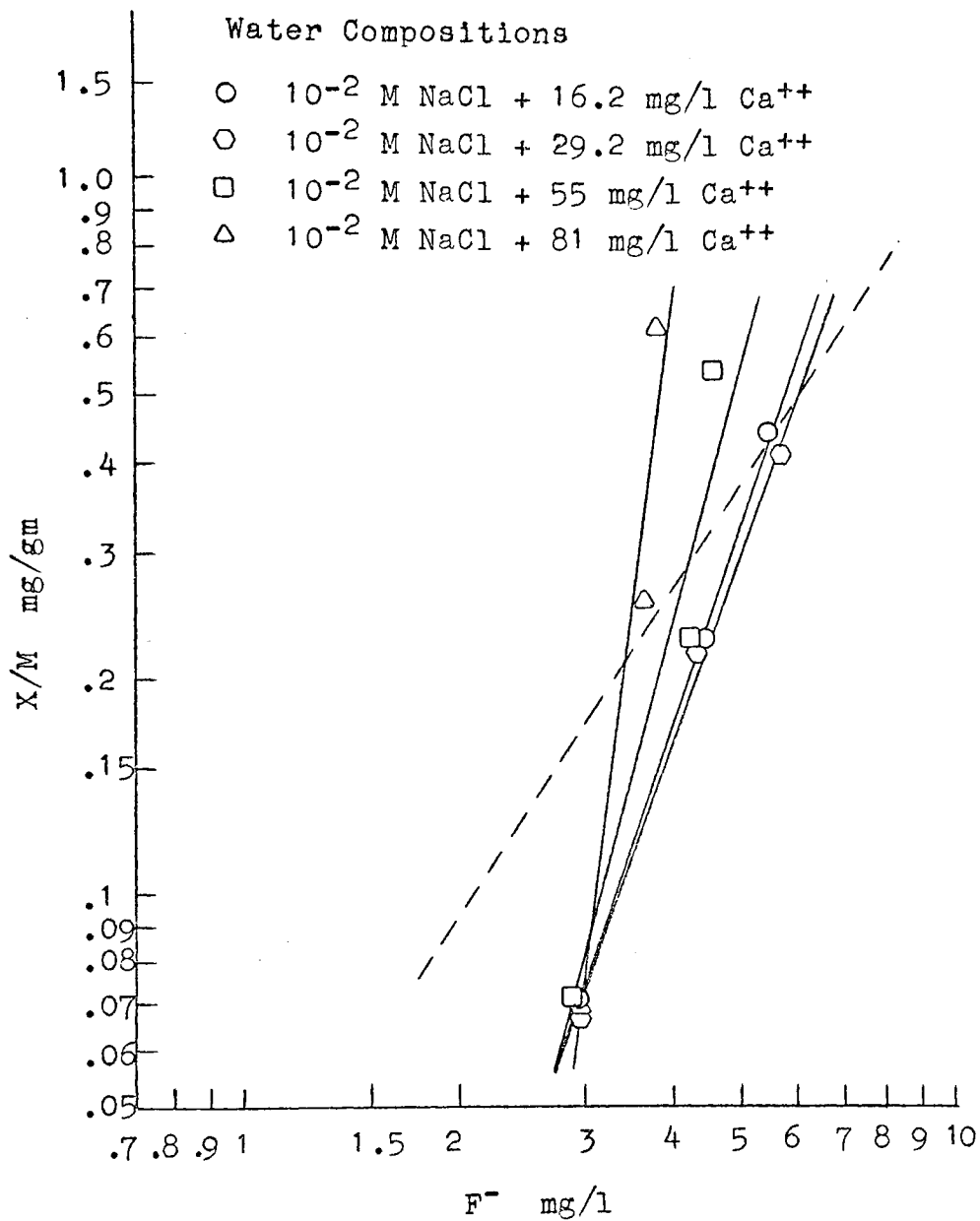


Fig. 20. Effect of Calcium Concentration on the Removal of Fluoride by Regenerated Activated Alumina

on the capacity is small. At higher equilibrium concentrations the effect of varying concentrations of Ca^{++} is larger and enhances adsorption. The highest concentration of calcium examined here is 2×10^{-3} M. The progressive clustering of the points as equilibrium concentration decreases indicates that the effects of the concentrations of calcium tested would be substantially the same at a 2 mg/l equilibrium concentration. At an equilibrium F^- concentration of 3 mg/l the capacity of the media in the presence of calcium in any concentration above 16 mg/l is 0.4 times that of the sodium chloride system. The variation in the effect of calcium at all concentrations over the range of equilibrium concentrations of fluoride and X/M values cannot be explained with the available data.

In Figure 21, the effects of sodium bicarbonate on fluoride sorption are illustrated. In order to eliminate ionic strength effects varying amounts of sodium chloride were added to keep the total number of charges in all systems constant, i.e., 10^{-2} M. The sodium ion concentration is constant in all systems. Sodium chloride concentrations are plotted at the top of Figure 21.

It is seen that the sorption capacity decreases in going from the left to the right of Figure 21 which means that the sorption capacity decreases with either increasing sodium bicarbonate concentration or decreasing sodium chloride concentration. In light of the data illustrated

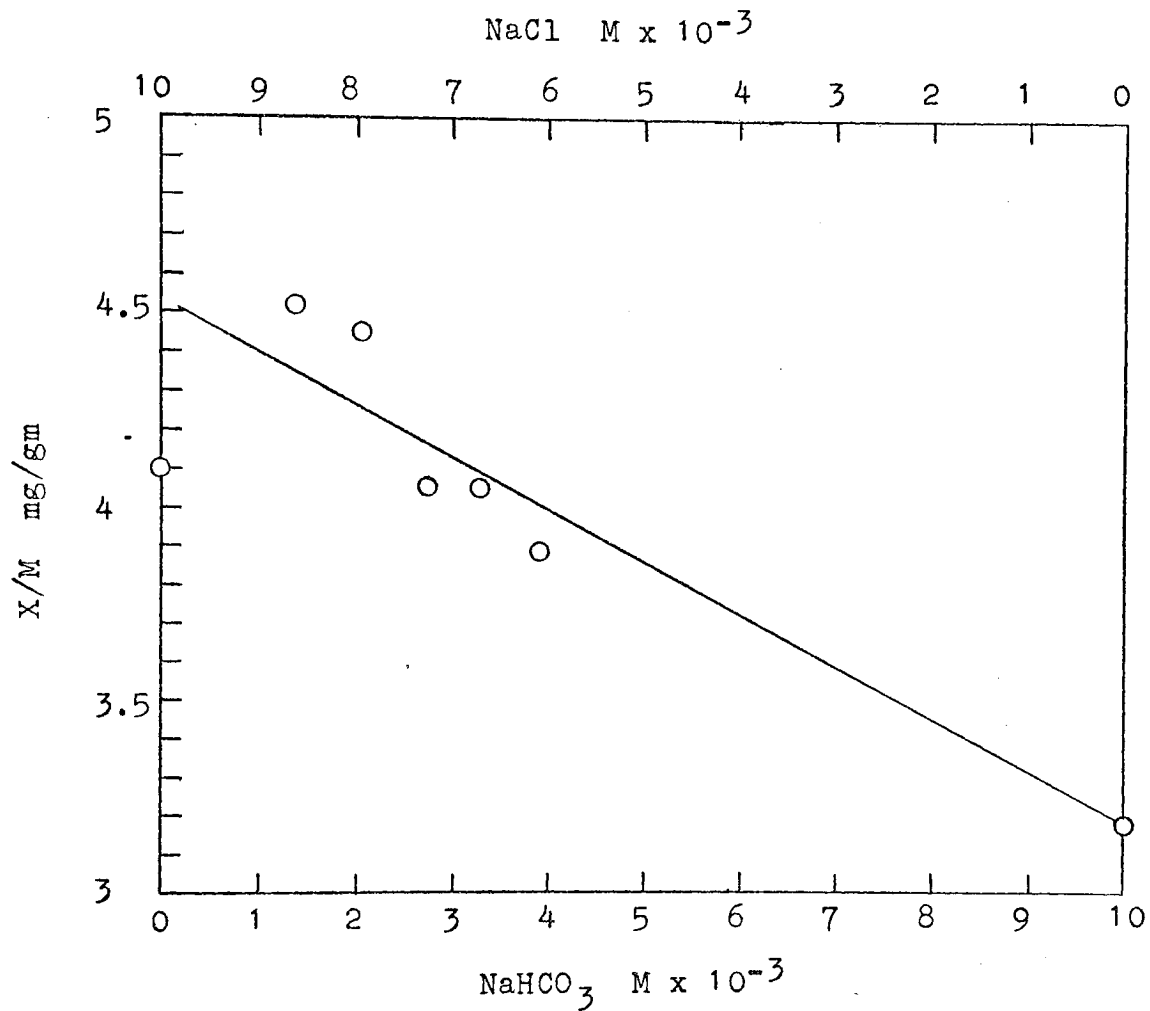


Fig. 21. Effect of Bicarbonate Concentration on Fluoride Sorption by Activated Alumina at Constant Mass of Media per Unit Volume (10 gm/l), Constant Ionic Strength, and from 10 mg/l F^-

in Figure 17 which indicates that sorption capacity decreases with increasing sodium chloride concentration, it can be concluded that the bicarbonate sorption interference is greater than the chloride sorption interference.

Tests were made to determine if the reduction in capacity associated with bicarbonate ion is due to the HCO_3^- ion or to a buffered high pH, Figure 22. Although the pH of the phosphate buffer, pH 7.7, was lower than that of the bicarbonate, pH 8.3, the results are comparable at higher equilibrium concentrations. At lower concentrations, the effect of bicarbonate is much stronger and is probably due to the higher pH.

Figure 23 is a display of the effects of 10^{-2} M potassium ion, 10 mg/l arsenic, and 22.8 mg/l silicate (SiO_2 from silicic acid). Over the entire range of fluoride equilibrium concentrations, it can be seen that the presence of these ions reduces the sorption capacity when compared to the sodium chloride system.

A comparison of F^- adsorption in a synthetic natural water, Table VI, a water with 29.2 mg/l Ca^{++} plus 166 mg/l HCO_3^- , and a water with 29.2 mg/l of calcium is shown in Figure 24. Again it is seen that calcium has the greatest effect on capacity.

A titration experiment was performed to attempt to separate the change in pH due to the media itself and the change in pH due to the ion exchange of hydroxyl for

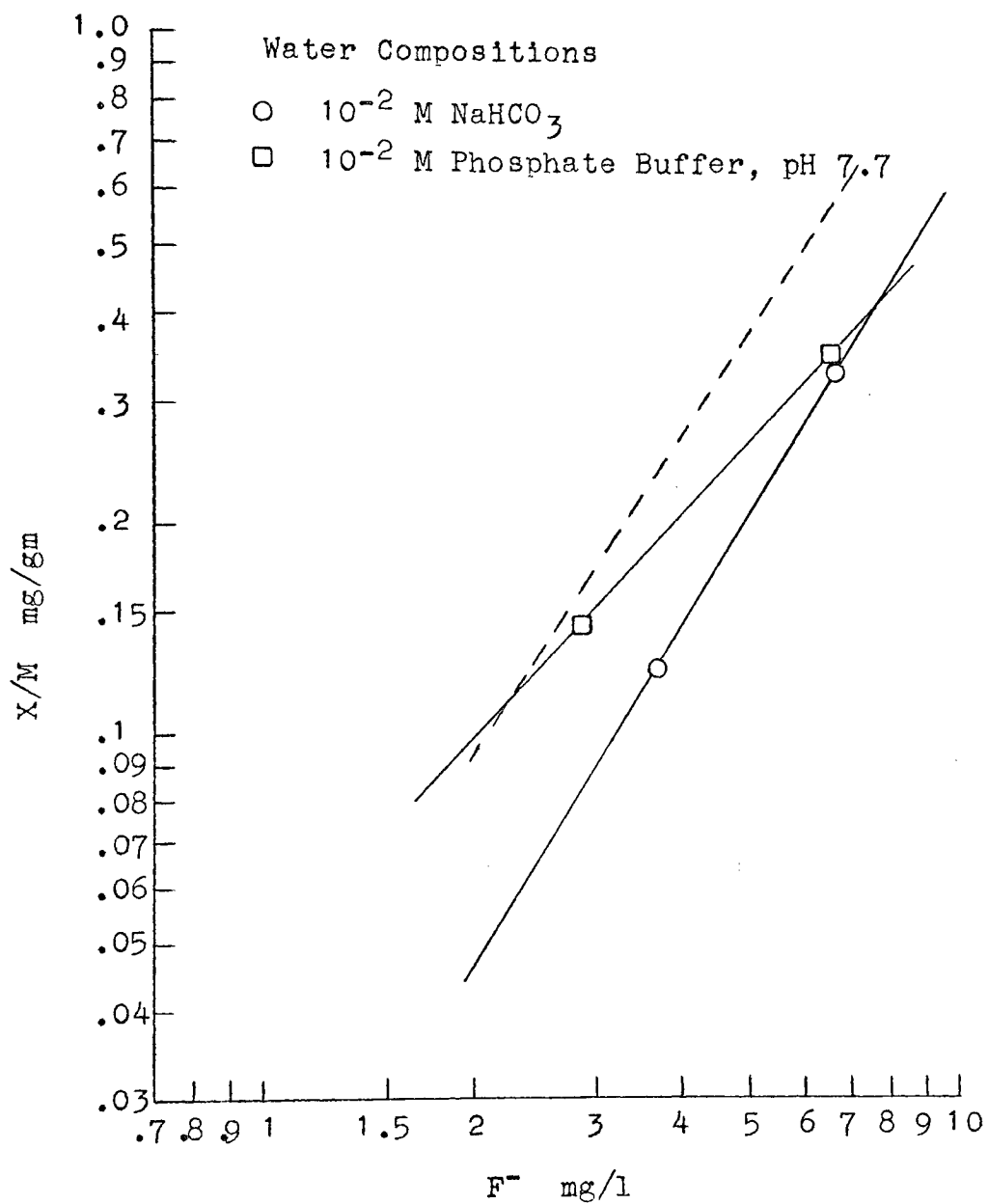


Fig. 22. Effect of 10^{-2} M Bicarbonate and 10^{-2} M Phosphate Buffer, pH 7.7, on Fluoride Removal by Regenerated Activated Alumina

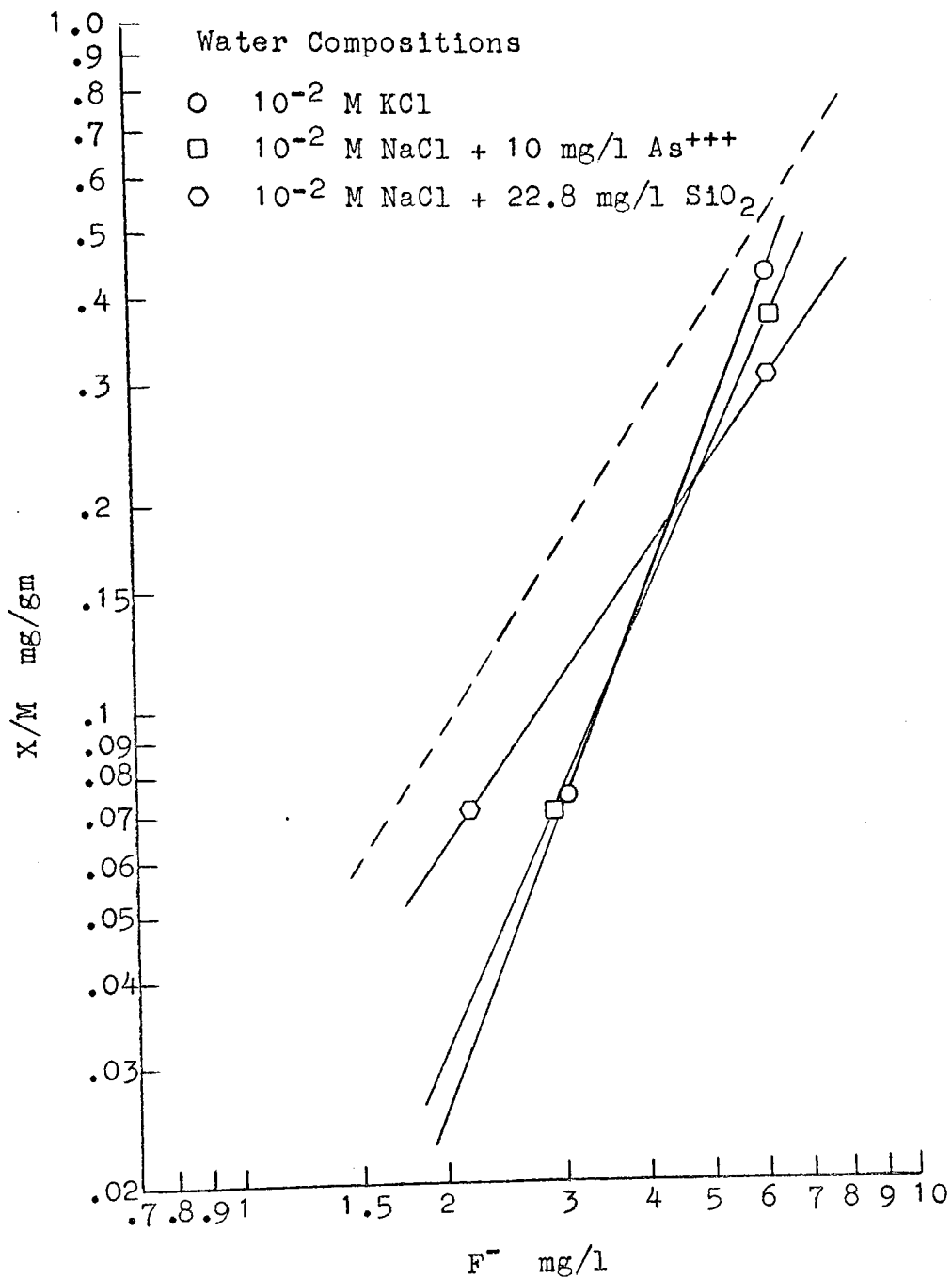


Fig. 23. Effect of 10^{-2} M KCl, 10 mg/l As^{+++} , and 22.8 mg/l SiO_2 on Fluoride Removal by Regenerated Activated Alumina

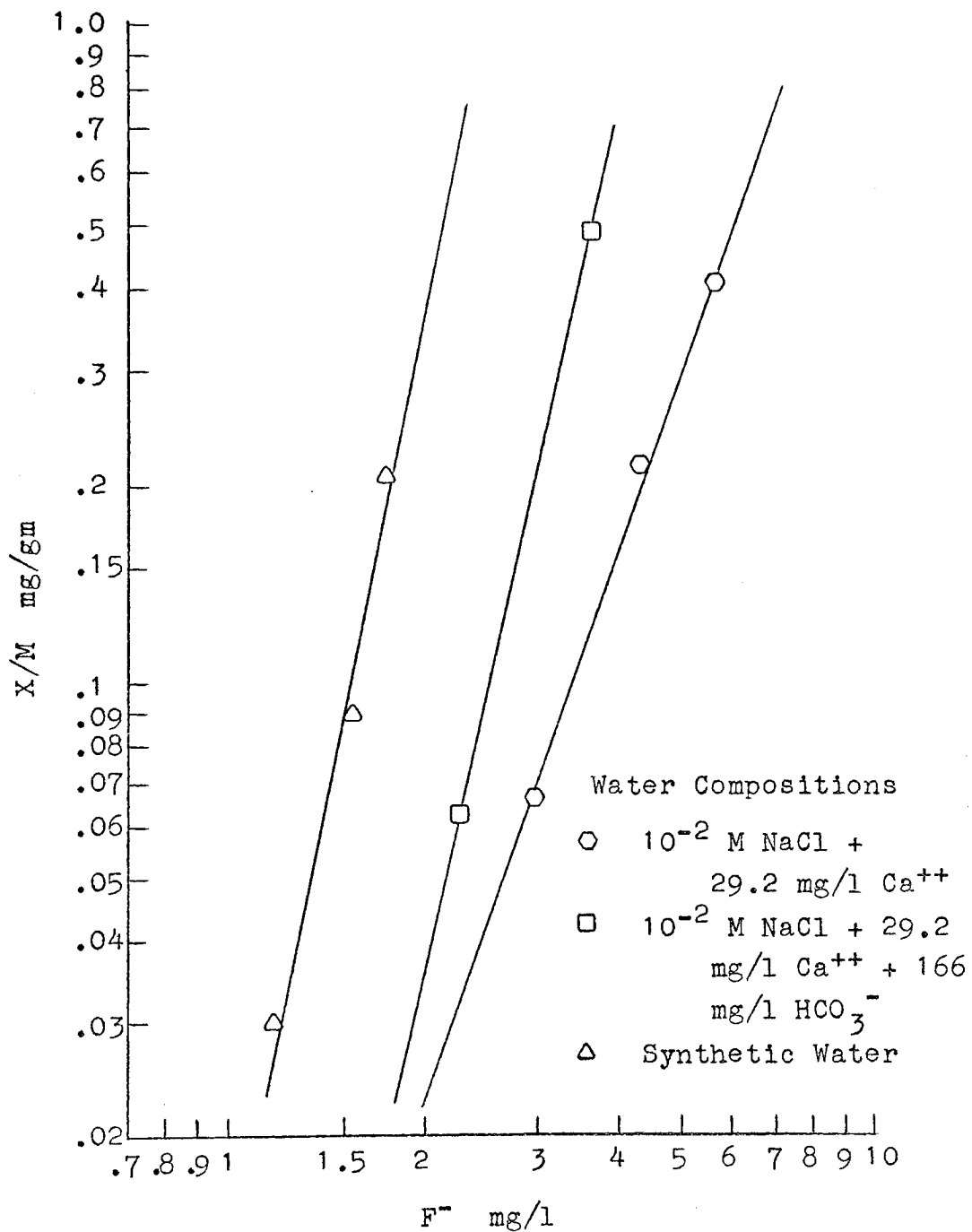


Fig. 24. Effect of Three Calcium Containing Waters on Fluoride Removal by Regenerated Activated Alumina

fluoride. Two 200 ml samples, each 10^{-2} NaCl, one with 9.1 mg/l F^- , Sample C, and the other with no fluoride, Sample D, were treated with 5 gm of activated alumina. The resulting pH of sample C was 10.1. It required 4.7×10.5 equivalents of acid to titrate 50 ml of sample C supernatant to pH 7. At equilibrium sample D was at pH 10.2. A 50 ml sample of supernatant required 4.9×10^{-5} equivalents of acid for titration to pH 7. The final concentration of fluoride in Sample D was 5.7 mg/l. For the 200 ml sample 0.7 mg (3.7×10^{-5} moles) of fluoride was removed. The difference in the titrations is 2.0×10^{-6} equivalents of hydroxide. It can be concluded that the removal process involves more than just ion exchange, since the equivalents of hydroxyl released is less than the equivalents of fluoride removed.

Discussion

A graphic representation of the effects of water composition on fluoride is presented in Figure 25 and 26. Capacities (X/M) are plotted against water components at constant equilibrium concentrations for fluoride. One mg/l of fluoride was chosen for the bone char illustration. The unavailability of data for equilibrium fluoride concentrations near 1.0 mg/l or less led to the choice of 2.0 mg/l as the equilibrium fluoride concentration in the activated alumina graph. These concentrations were chosen

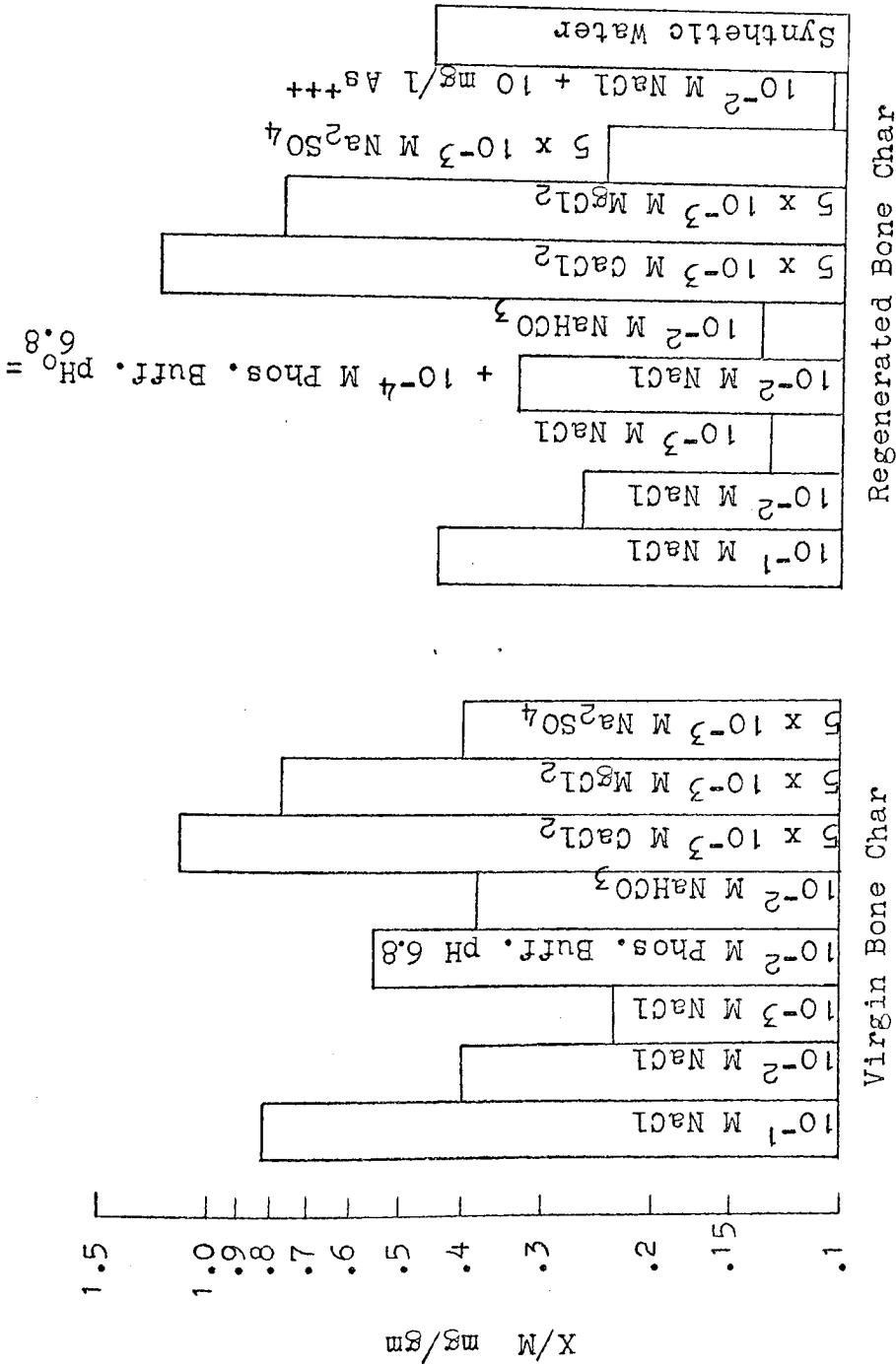


Fig. 25. Comparison of Capacities of Virgin and Regenerated Bone Char at 1.0 mg/l Fluoride Equilibrium Concentration for Selected Water Components.

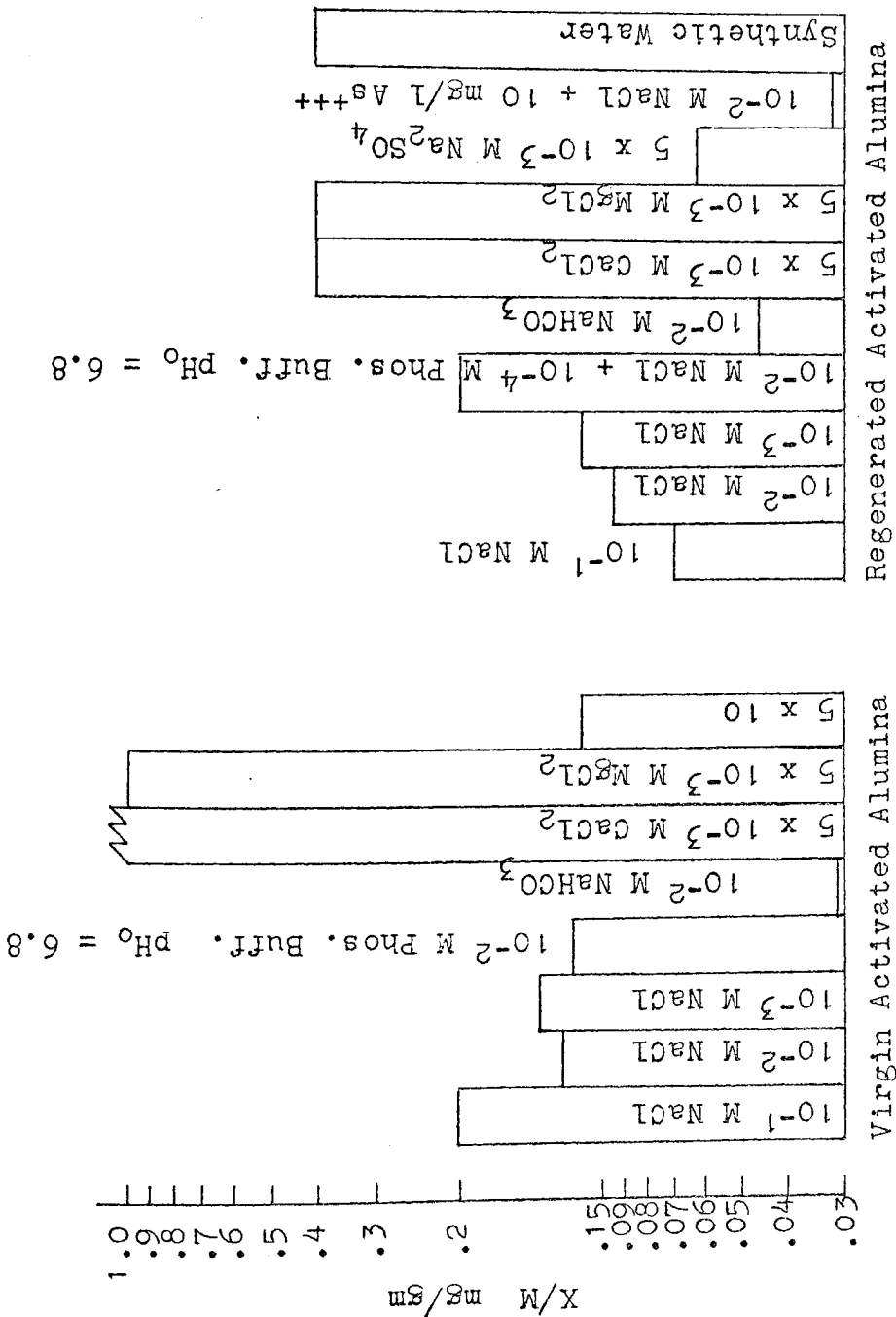


Fig. 26. Comparison of Capacities of Virgin and Regenerated Activated Alumina at 2.0 mg/l Fluoride Equilibrium Concentration for Selected Water Components

because they are realistic goals for equilibrium fluoride concentration in fluoride removal processes. Both of these concentrations can be considered valid.

Removal of fluoride from natural waters is influenced by several factors. The data show that pH, ionic strength, and water composition all have effects on the removal capacities of the media. Experiments have also indicated that both media increase the pH when they are added to aqueous solutions. When 10 grams of virgin media were added to 200 ml of 10^{-2} M NaCl, the resulting pH's were 7.87 for bone char and 8.25 for activated alumina. The pH changes were not instantaneous but occurred about 10 minutes after the addition of the media. Two grams of regenerated bone char in 200 ml of 10^{-2} M NaCl raised the pH to 8.4. Five grams of regenerated activated alumina raised the pH of 200 ml of 10^{-2} M NaCl to 10.1. These pH increases must be considered in any fluoride removal process utilizing these media.

Increased ionic strength may suppress the boundary layer of adhered water molecules on the surface of the media allowing the fluoride ion to approach closer to the surface where it reacts. Since the reaction is apparently one of ion exchange hydroxide ion competes with fluoride ions for the sorption sites at high values of pH.

The greater removal and higher capacity of the media for fluoride in the presence of calcium may be

explained, in part, by the low solubility of CaF_2 . A table of thermodynamic data applicable to aqueous fluoride chemistry is presented in Appendix B. When 10 mg/l F^- is present in a 5×10^{-3} M Ca^{++} solution, CaF_2 precipitates and reduces the fluoride concentration to 3.55 mg/l and the calcium to 4.88×10^{-3} M. The sorption media is then exposed to a solution containing the 3.55 mg/l of F. The removal is from 3.55 mg/l and not 10 mg/l. The rate of precipitation is effected by the presence of nucleation sites. In a column, the first media encountered by the water would serve as the nucleation sites. In case of magnesium, the equilibrium constant is such that an initial fluoride concentration of 10 mg/l is in equilibrium with 5×10^{-3} M Mg^{++} . The results indicate that there is either a complexing reaction between the media and the divalent metal ions or a precipitation of the metal fluoride at the surface of the media. The precipitated material would necessarily have to remain at the surface, probably attached by electrical or Van der Waals forces, otherwise, in the bulk liquid some would dissociate to maintain concentrations commensurate with the solubility product and the result in fluoride concentrations in excess of those measured.

It is apparent that both the precipitation of fluoride and ion exchange for fluoride are working simultaneously. Lower final pH values for the cases where

divalent metal ions are present lends credence to this explanation, Table VII. In cases where pH is greater than 8.0 to 8.3, depending on the concentration of Ca^{++} , CaCO_3 will precipitate. When CO_3^- is present and the pH is greater than 10.0, both $\text{Mg}(\text{OH})_2$ and CaCO_3 will precipitate. Such precipitations are also influenced by the presence of nucleation sites, namely the surface of the adsorption or exchange media. High concentrations of hydroxyl at the surface of the media also influence the effective pH at the surface and hence the precipitation. With prolonged use, precipitated compounds may poison the bed by remaining attached to the media after regeneration.

Bicarbonate or other high pH causing species inhibit the fluoride removal by both media in either the raw or virgin state. The buffering capacity of the waters must be determined with respect to the initial pH and the amount of fluoride to be removed. Initial pH by themselves have little meaning.

There is evidence that a relationship exists between the isotherm results and the full scale plant operating characteristics. The bone char plant at Britton is reported to have a capacity of 1.14 gm/kg when treating a 3.0 mg/l fluoride water. Since at the time the average fluoride concentration of the effluent over the run becomes equal to the desired value, most of the column will be saturated with fluoride. The results of the experiments

TABLE VII

COMPARISON OF INITIAL & FINAL pH'S IN THE
PRESENCE OF DIVALENT METAL IONS

Sample	Water Comp.	Gm Media/l	F _o	F _f	pH	pH _f
<u>Virgin Bone Char</u>						
1	10 ⁻² M NaCl	2.5	9.8	6.3	6.4	7.6
2		15	9.8	2.0	6.4	8.5
3	5 x 10 ⁻³ M MgCl ₂	2.5	9.5	4.7	6.2	7.2
4		15	9.5	.6	6.2	7.7
5	5 x 10 ⁻³ M CaCl ₂	2.5	9.8	3.4	6.6	7.1
6		15	9.8	.4	6.6	7.5
<u>Virgin Activated Alumina</u>						
7	10 ⁻² M NaCl	15	9.8	4.6	6.4	9.1
8		75	9.8	2.0	6.4	9.9
9	5 x 10 ⁻³ M MgCl ₂	15	9.5	1.7	6.2	7.7
10		75	9.5	.9	6.2	9.0
11	5 x 10 ⁻³ M CaCl ₂	15	9.8	1.5	6.6	7.3
12		75	9.8	1.5	6.6	9.0
<u>Regenerated Bone Char</u>						
13	10 ⁻² M NaCl	2.5	9.7	6.5	6.0	7.2
14		25	9.7	1.4	6.0	8.2
15	5 x 10 ⁻³ M MgCl ₂	2.5	9.1	4.7	5.8	7.0
16		25	9.1	.4	5.8	7.9
17	5 x 10 ⁻³ M CaCl ₂	2.5	9.3	4.7	6.3	6.5
18		25	9.3	.4	6.3	7.5
<u>Regenerated Activated Alumina</u>						
19	10 ⁻² M NaCl	10	9.7	5.6	6.0	9.0
20		50	9.7	2.7	6.0	9.6
21	5 x 10 ⁻³ M MgCl ₂	10	9.1	2.9	5.8	8.3
22		50	9.1	2.6	5.8	8.8
23	5 x 10 ⁻³ M CaCl ₂	10	9.3	2.4	6.3	8.3
24		50	9.3	2.4	6.3	9.5

with the synthetic water indicate that at an equilibrium level of 3.0 mg/l fluoride, the capacity (X/M) is 1.1 gm/kg. By extrapolating the synthetic water curve to an equilibrium of 8 mg/l, the X/M is 2.5 gm/kg. The experience at Britton with a water of 8.0 mg/l of fluoride showed a capacity of 2.0 gm/kg.

The results of the experiments with activated alumina are not expected to compare well with the experience at Bartlett because of the difference in the regeneration methods. The Bartlett plant uses countercurrent column regeneration while batch regeneration was used in the laboratory. The plant results are 1.77 gm/kg for a run average of 1.0 mg/l F^- effluent from a raw water concentration of 8.1 mg/l. Extrapolation of the curve for the synthetic water in Figure 24 gives removal loadings of this same magnitude.

CHAPTER 6

DESIGN CONSIDERATIONS

The selection of media for a fluoride removal installation should be based on factors of water composition, expense of media, and regeneration characteristics of the media. From the data presented here, test columns can be designed to give more complete data for the system being treated. Bone char columns can be designed with this data. The data for virgin activated alumina and regenerated activated alumina at the levels of regeneration achieved in this study are suitable for use in design. The relative cost of the media and regeneration must be balanced against the removal capacities to give an economic design.

Several water composition parameters indicate the direction the designer should take. If the water has a very high TDS, bone char is favored. Highly alkaline waters have a lower effluent pH from bone char treatment than from activated alumina treatment. Acidification of the water before treatment may make activated alumina the media of choice, however, the effect of the acid addition on the TDS will have to be considered. If the increase in

TDS is excessive, a substantial decrease in the removal capacity for fluoride will occur.

Addition of calcium to waters of low hardness can be considered to improve the removal capacity. Alkalinity of the water in the form of carbonate species and the pH changes during the run of a column must be considered in order to prevent precipitation of CaCO_3 . There is evidence in the literature (22, 27) that calcium (hardness) is taken out during the course of a column run. Near the end of the run, the calcium of the effluent is nearly the same as that of the influent.

Arsenic in a high fluoride water necessitates the use of activated alumina because arsenic causes irreversible changes in the composition of bone char (37).

For a very high fluoride water (20 mg/l or more) columns in series should provide the lowest cost treatment. The first column can be run to exhaustion while the second serves as a polishing column. Alternate regeneration and control of the flow through the columns can produce an effluent with the desired average fluoride concentration and allow greater sorption loadings of the media to be attained. Acidification at one or more points may be necessary to keep the pH down and to increase removals and/or prevent precipitation of metal carbonates or hydroxides.

If single pass units are to be designed, activated alumina seems to be the media of choice. It will probably

be necessary to prepare the virgin material for single pass usage by a regeneration technique. Waters treated with raw bone char have a greasy scum which was not apparent in water treated with the regenerated media. The number of regenerations to rid the char of the grease is not known.

One large problem remains in the defluoridation of drinking waters, namely that of the individual or small community supply. The research reviewed in this paper indicates the feasibility of a rechargeable unit with interchangeable media cartridges which could be regenerated at a facility central to the individual installations. The evidence gathered by Savinelli and Black (22) indicates that it may be feasible to regenerate individual units of activated alumina with the caustic soda method followed by an alum rinse. It is not economical to regenerate with alum alone since 10 times the mass of alum compared to sodium hydroxide is used. With the relative cost of alum being $1/2$ that of sodium hydroxide, a 3 to 4 fold increase in capacity is coupled with a five fold increase in cost for regenerant.

Laboratory studies of fluoride removal using activated alumina should be conducted with media which has been regenerated in a column mode where each successive volume of regenerant or rinse can displace the last one to insure complete removal of fluoride ions released by the caustic solution.

CHAPTER 7

CONCLUSIONS

The following major conclusions can be made from the laboratory and literature research which is presented herein:

1. Hardness ions, specifically magnesium and calcium enhance removal.
 - a. The CaF_2 and MgF_2 precipitate at concentrations near those found in high fluoride waters.
 - b. The media provide nucleation sites for the precipitation.
 - c. Lower effluent pH's are experienced compared to waters with no hardness.
 - c. Higher loadings are achieved.
2. Initial pH's between 5 and 9 affect fluoride removal to a small degree.
3. The presence of bicarbonate reduces removal and affects the equilibrium pH.
4. For virgin, and regenerated bone char as well as virgin activated alumina the presence of chloride increases removal over that of just

fluoride in distilled water. Thus, higher ionic strengths assist removal.

5. Higher ionic strengths decrease removal of fluoride by regenerated activated alumina.
6. Potassium, nitrate, and sulfate ions do not appreciably affect the removal of fluoride, although they do contribute to the ionic strength of the water. In most cases nitrate and potassium have very low concentrations in most Arizona groundwaters with high F^- concentration.
7. Arsenic inhibits fluoride removal.
8. Both media can be regenerated in flasks.
 - a. Bone char recovers its effectiveness.
 - b. Activated alumina retains a considerable amount of fluoride.
9. A typical fluoride water composition was established from Arizona well water data. Means and standard deviations for major components of Arizona waters with more than 1.4 mg/l of fluoride and less than 1000 mg/l of total dissolved solids were presented and used in the laboratory work.
10. Suggestions for application of the results to design were presented.

APPENDIX A

COMPUTER STUDY

A computer program was developed to give statistical data to aid in the experimental design for the laboratory work done in this investigation. The program was written in the Fortran IV Language (38) and executed on the University of Arizona CDC 6500 machine.

The purposes of this program were to select waters of certain fluoride concentrations and certain total dissolved solids from existing water quality data, find the means and standard deviations of the major components of these waters and to find correlation coefficients between the components. The water quality data of Dutt and McCreary (14) was available on computer cards and used as input.

The block flow chart for the program is presented in Figure 27. Results of the program are presented in Tables VIII through XVIII.

Discussion

The only substantial correlations of components of high fluoride waters were between sodium and chloride, and carbonate and pH. None of the values are high enough to warrant much attention. The conclusion is that the

composition of water is independent of any one variable of water composition. Hence, design of experiments concerning high fluoride water compositions must be done to include the independence of the components under study.

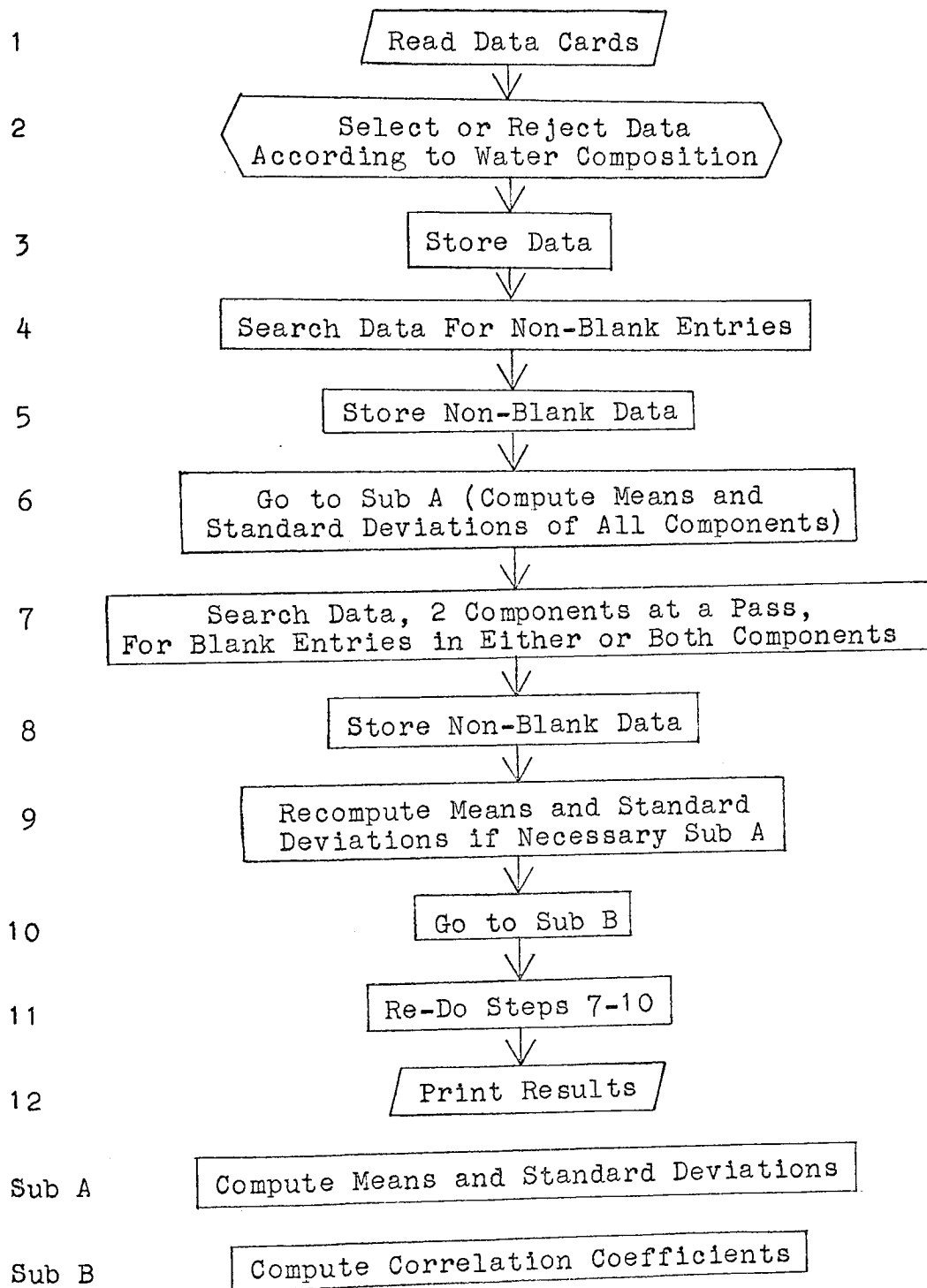


Fig. 27. Operational Block Flow Chart
for Computer Program

TABLE VIII
 MEANS AND STANDARD DEVIATIONS
 OF ARIZONA WATER COMPONENTS

F \geq 0 mg/l TDS \geq 0 mg/l All Available Data 828 Points		
Component	μ mg/l	σ mg/l
Calcium	75	79
Magnesium	18	24
Sodium	134	190
Chloride	147	283
Sulfate	170	251
Bicarbonate	200	134
Carbonate	.7	2.84
Fluoride	1.6	2.4
Nitrate	9.5	15
pH	7.8	.44
Potassium	3.8	3.0
Boron	.4	2.0
Silicate	54	442

TABLE XI
CORRELATION COEFFICIENTS OF HIGH
FLUORIDE WATER COMPONENTS
 F^2 vs. Mg, Ca

$F^- \geq 1.4$	$TDS \leq 1000$	147 Data Points
Component		F^2
Calcium		-.211
Magnesium		-.028

TABLE XII
CORRELATION COEFFICIENTS OF HIGH FLUORIDE WATER COMPONENTS

Component	F ⁻ ≥ 2 mg/l		TDS ≤ 1000 mg/l							111 Data Points				
	μg/l	σ ² mg/l	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F	NO ₃	pH	K	B	SiO ₂
Calcium	31.1	29.3	.681	-.114	.188	.457	.287	-.419	-.295	.386	-.543	.112	-.159	-.112
Magnesium	7.8	8.1		-.144	.011	.378	.613	-.366	-.103	.265	-.543	.321	-.213	-.103
Sodium	116.5	67.0		.815		.495	-.120	.102	.231	.082	.234	.247	.587	-.092
Chloride	79.5	81.0				.455	-.245	-.139	.006	.147	-.028	.268	.494	-.168
Sulfate	112.0	80.6				-.025	-.116		.375	.293	-.231	.523	.195	-.169
Bicarbonate	157.7	74.8						-.273	-.124	.042	-.322	.089	-.150	.136
Carbonate	2.8	5.7							.226	-.213	.755	-.233	.050	-.059
Fluoride	4.9	4.0								-.028	.108	.445	.136	.159
Nitrate	5.0	6.2									-.358	.223	.143	.055
pH	8.1	.6										-.415	.126	.032
Potassium	3.5	2.7											.168	-.072
Boron	.4	.6												0.130
Silicate	23.8	13.0												

TABLE XIII

CORRELATION COEFFICIENTS OF HIGH FLUORIDE WATER COMPONENTS

Components	F ⁻ ≥ 3 mg/l		TDS ≤ 1000 mg/l										72 Data Points				
	μ mg/l	σ mg/l	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F	NO ₃	pH	K	B	SiO ₂			
Calcium	23.5	24.1	.640	-.132	.125	.341	.215	-.428	-.205	.587	-.590	.132	-.140	-.071			
Magnesium	5.9	7.3		-.070	.016	.386	.637	-.342	.083	.347	-.341	.427	-.188	-.071			
Sodium	113.7	67.9			.833	.454	-.065	.027	.096	.070	.183	.186	.594	-.204			
Chloride	87.6	83.4				.384	-.252	-.189	-.073	.134	-.064	.221	.543	-.261			
Sulfate	119.5	77.9					-.024	-.174	-.472	.408	-.306	.576	.184	-.214			
Bicarbonate	143.9	76.0					-.194		.001	.028	-.242	.161	-.154	.192			
Carbonate	3.8	6.2							.149	-.286	.725	-.275	-.015	-.094			
Fluoride	6.3	4.4								-.107	.001	.458	.014	.115			
Nitrate	5.4	6.2									-.457	.194	.126	-.053			
pH	8.2	.7										-.488	.081	-.007			
Potassium	3.8	3.1											.143	-.134			
Boron	.5	.7												-.170			
Silicate	25.2	15.0															

TABLE XIV
CORRELATION COEFFICIENTS OF HIGH FLUORIDE WATER COMPONENTS

Component	F ⁻ ≥ 4 mg/l		TDS ≤ 1000 mg/l							59 Data Points				
	μg/l	σ ² mg/l	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F	NO ₃	pH	K	B	SiO ₂
Calcium	21.6	23.3	.574	-.083	.215	.373	.013	-.435	-.177	.597	-.587	.151	-.131	-.049
Magnesium	5.2	6.5		-.078	.067	.427	.527	-.322	.210	.304	-.571	.545	-.214	.041
Sodium	140.5	67.1			.818	.402	-.024	.101	.021	-.000	.223	.132	.596	-.183
Chloride	94.4	85.4			.340	-.230	-.182	-.158	.448	.376	-.324	.168	.532	-.291
Sulfate	128.2	79.8			.051	-.122			.122	-.030	-.170	.240	-.144	.336
Bicarbonate	134.5	69.1				-.074			.227	-.288	.718	-.299	-.021	.146
Carbonate	3.5	5.6								-.132	-.027	.452	-.025	.184
Fluoride	7.0	4.5									-.466	.177	.119	-.034
Nitrate	5.5	6.3										-.519	.083	.010
pH	8.2	.7											.116	-.116
Potassium	3.9	3.3												.142
Boron	.5	.7												
Silicate	24.6	14.3												

TABLE XV
CORRELATION COEFFICIENTS OF HIGH FLUORIDE WATER COMPONENTS

Component	F ⁻ ≥ 5 mg/l		TDS ≤ 1000 mg/l											35 Data Points				
	μ mg/l	σ mg/l	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F	NO ₃	pH	K	B	SiO ₂				
Calcium	16.3	18.6	.467	-.191	.098	.399	-.156	-.447	-.080	.827	-.590	.203	-.059	-.062				
Magnesium	4.5	6.1		-.242	-.128	.599	.371	-.383	.432	.357	-.705	.788	-.215	-.007				
Sodium	148.1	66.2			.789	.316	.032	.102	-.086	-.046	.223	.006	.648	-.177				
Chloride	85.8	74.7				.269	-.255	-.217	-.179	.117	-.107	.112	.746	-.302				
Sulfate	171.7	87.2					.043	-.146	.469	.371	-.372	.641	.079	-.169				
Bicarbonate	135.6	69.8						-.098	.157	-.106	-.183	.281	-.142	.320				
Carbonate	4.7	6.5							.142	-.300	.712	-.317	-.104	-.173				
Fluoride	8.9	5.1								-.167	-.164	.517	-.185	.155				
Nitrate	5.3	6.8									-.429	.096	.085	-.050				
pH	8.3	.8										-.599	.017	.062				
Potassium	4.2	3.9											.012	-.115				
Boron	1.7	.8												-.135				
Silicate	26.2	17.2																

TABLE XVI
CORRELATION COEFFICIENTS OF HIGH FLUORIDE WATER COMPONENTS

Component	F ⁻ ≥ 6 mg/l		TDS ≤ 1000 mg/l										24 Data Points				
	Ca mg/l	σ ² mg/l	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F	NO ₃	pH	K	B	S102			
Calcium	13.4	10.6	.533	-.010	.400	.467	-.084	-.672	.096	.458	-.792	.542	.118	-.198			
Magnesium	4.7	6.5		-.339	-.170	.575	.351	-.454	.532	.402	-.742	.828	-.241	-.147			
Sodium	160.0	70.0			.773	.275	-.036	.029	-.287	.275	.191	-.113	.643	-.299			
Chloride	94.3	83.7			.285	-.335	-.261	-.325	.380	-.130	.051	.743	-.395				
Sulfate	153.6	86.6				.067	-.283	.517	.532	-.478	.763	.070	-.342				
Bicarbonate	138.0	73.6					-.165	.163	.099	-.218	.189	-.191	.248				
Carbonate	5.5	7.3						.048	-.385	.726	-.364	-.130	-.176				
Fluoride	10.6	5.4							.033	-.266	.589	-.317	-.176				
Nitrate	3.7	3.1								-.494	.316	.371	-.174				
pH	8.4	.9									-.656	-.025	.072				
Potassium	4.4	4.4										-.065	-.239				
Boron	.8	.9											0.200				
Silicate	26.3	19.5															

TABLE XVII
CORRELATION COEFFICIENTS OF HIGH FLUORIDE WATER COMPONENTS

Component	F ⁻ ≥ 7 mg/l		TDS ≤ 1000 mg/l										20 Data Points				
	μ/L mg/l	σ ⁻ mg/l	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F	NO ₃	pH	K	B	SiO ₂			
Calcium	13.1	11.6	.552	.000	.433	.506	0.107	-.684	.124	.588	-.810	.557	.124	-.196			
Magnesium	4.7	6.9		-.352	-.139	.644	.293	-.475	.574	.389	-.728	.883	-.240	-.168			
Sodium	167.0	72.5			.777	.183	-.004	-.027	-.388	.311	.185	-.178	.622	-.346			
Chloride	102.1	87.8				.252	-.269	-.358	-.442	.606	-.200	-.005	.734	-.430			
Sulfate	156.6	88.9					.113	-.352	.554	.617	-.542	.784	.007	-.413			
Bicarbonate	132.9	63.9						-.126	.287	-.340	-.098	.332	-.181	.243			
Carbonate	6.5	7.7							-.055	-.427	.744	-.442	-.198	-.176			
Fluoride	11.4	5.5							.113		-.314	.575	-.418	.188			
Nitrate	3.5	2.7									-.490	.466	.502	-.335			
pH	8.4	.9										-.716	-.049	.097			
Potassium	4.7	4.7											-.121	-.249			
Boron	1.8	1.0															
Silicate	26.3	21.7												-.221			

TABLE XVIII
CORRELATION COEFFICIENTS OF HIGH FLUORIDE WATER COMPONENTS

Component	F ⁻ ≥ 8 mg/l		TDS ≤ 1000 mg/l							13 Data Points				
	μg/l	Cl ⁻ mg/l	Mg	Na	Cl	SO ₄	HCO ₃	CO ₃	F	NO ₃	pH	K	B	SiO ₂
Calcium	9.5	10.4	.765	-.391	-.037	.695	.090	-.663	.606	.701	-.853	.779	-.259	-.161
Magnesium	5.2	8.2		-.290	.051	.750	.192	-.575	.654	.778	-.830	.875	-.148	-.235
Sodium	148.2	72.6			.785	.130	.406	.170	-.299	-.145	.428	-.137	.703	-.339
Chloride	59.7	50.1				.479	.361	-.119	-.158	.204	.065	.218	.673	-.618
Sulfate	169.8	102.3					.222	-.485	.584	.835	-.604	.824	.060	-.532
Bicarbonate	146.5	68.0						-.337	.163	-.065	-.245	.309	.585	.177
Carbonate	8.9	8.5							-.398	-.425	.735	-.542	-.023	-.275
Fluoride	13.7	5.6								.575	-.589	.606	-.421	.096
Nitrate	2.7	2.4									-.614	.791	-.220	-.394
pH	8.6	1.1										-.794	.190	.056
Potassium	5.2	5.8											.006	-.318
Boron	.4	.4												-.237
Silicate	29.4	27.8												

APPENDIX B

THERMODYNAMICS OF FLUORIDE IN AQUEOUS SOLUTION

Computation of equilibrium constants are made according to the following formulas and concepts. The free energy of formation of a reaction is found by subtracting the free energy of formation of the reactants from the free energy of the product of the reaction. In symbols, this is

$$\Delta F^{\circ}_{\text{Rxn}} = \Delta F^{\circ} \text{ Products} - \Delta F^{\circ} \text{ Reactants}$$

where ΔF° is the free energy of formation of the compound, ion, or reaction.

The equilibrium constant is computed from

$$\Delta F^{\circ}_{\text{Reaction}} = -RT \ln k$$

where R = universal gas constant

T = absolute reaction temperature

k = equilibrium constant.

In the case where T = 298.18°k,

$$\Delta F^{\circ}_{\text{Reaction}} = -136.4 \log k,$$

Table XIX presents some thermodynamic data relevant to computations which may be made for reactions involving fluoride.

Table XX lists some equilibrium constants computed from thermodynamic data or listed by various authors.

Figure 28 illustrates the equilibrium curves for CaF_2 using two values for the equilibrium constant.

TABLE XIX

THERMODYNAMIC DATA FROM LATIMER (39)

Heat and free energy of formation in Kcal.
 Entropy of substance in cal/deg C. Values
 estimated by Latimer in parentheses.

Formula	State	ΔH°	ΔF°	ΔS°
Al ⁺⁺⁺	aq	-125.4	-115.0	-74.9
AlF ₃	c	-311.	-294.	23.
AlF ₆ ⁻⁻⁻	aq		-539.6	(-40.)
AlO ₂	aq	-218.6(?)	-204.7	(25.)
Al ₂ O ₃	corundum c	-399.09	-376.77	12.186
Al ₂ O ₃ ·H ₂ O	c	-471.	-435.	23.15
Al ₂ O ₃ ·3H ₂ O	hydragillete	-613.7	-547.9	33.51
Al(OH) ₂	amorph.	-304.9	-271.9	(17.)
Ca ⁺⁺	aq	-129.77	-132.18	-13.2
CaCO ₃	aragonite ^c	-288.49	-269.53	21.2
Ca(OH) ₂	c	-235.8	-214.33	18.2
CaF ₂	c	-290.3	-277.7	16.46
Cl ⁻	aq	-40.023	-31.350	13.2
ClO ⁻	aq		-8.9	10.0
CO ₃ ⁼	aq	-161.63	-126.22	-12.7
F ⁻	aq	-78.66	-66.08	-2.3
H ⁺	aq	0.0	0.0	0.0
H ₂ AlF ₆	aq	-597.2		
HCO ₃ ⁻	aq	-165.18	-140.31	22.7
HF	aq	-78.66	-70.41	26.

TABLE XIX, Continued

Formula	State	ΔH°	ΔF°	ΔS°
HF_2^-	aq	153.6	-137.5	0.5
H_2O	liq	-68.317	-56.690	16.716
HOCl	aq	-27.83	-19.110	31
H_2SiO_3	c	-270.7	-244.5	
K^+	aq	-60.04	-67.46	24.5
KF	c	-134.46	-127.42	15.91
$\text{KF}\cdot 2\text{H}_2\text{O}$	c	-277.00	-242.7	36.
KHF_2	c	-219.98	203.73	24.92
KOH	c	-101.78	-89.5	(14.2)
Mg^{++}	aq	-110.41	-108.99	-28.2
MgCO_3	c	-266.	-246.	15.7
MgF_2	c	-263.5	-250.8	13.68
$\text{Mg}(\text{OH})_2$	c	-221.00	-199.27	15.09
Na^+	aq	-57.279	-62.589	14.4
NaF	c	-136.0	-129.3	14.0
NaF	aq	-135.94	-128.67	12.1
NaHF_2	c	-216.6		
NaHCO_3	c	-226.5	-203.6	24.4
NaOH	aq	-112.236	-100.184	11.9
$\text{NaOH}\cdot\text{H}_2\text{O}$	c	-175.17	-149.00	20.2
NO_3^-	aq	-49.372	-26.43	35.0
OCl^-	aq		-8.9	10.0

TABLE XIX, Continued

Formula	State	ΔH°	ΔF°	ΔS°
OH^-	aq	-54.957	-37.595	-2.52
PO_4^{3-}	aq	-306.9	-245.1	152.
$\text{SO}_4^{=}$	aq	-216.90	-124.0	(8.)
SiF_6^{--}	aq	-558.5	-511.	12.(?)
Sn^{++}	aq	-2.39	-6.275	-5.9
SnF_2				
SnF_6^{--}	aq	-474.7	-420.0	(0.)
$\text{Sn}(\text{OH})_2$	c	-138.3	-117.6	23.1

TABLE XX
EQUILIBRIUM CONSTANTS FOR REACTIONS
INVOLVING FLUORIDE

Reaction	Constant	Reference
$\text{AlF}^{++} \rightarrow \text{Al}^{+++} + \text{F}^-$	$k_1 = 7.4 \times 10^{-7}$	(39)
$\text{AlF}_2^+ \rightarrow \text{Al}^{+++} + 2\text{F}^-$	$k_2 = 7.1 \times 10^{-12}$	(39)
$\text{AlF}_3 \rightarrow \text{Al}^{+++} + 3\text{F}^-$	$k_3 = 1.0 \times 10^{-15}$	(39)
$\text{AlF}_4^- \rightarrow \text{Al}^{+++} + 4\text{F}^-$	$k_4 = 1.8 \times 10^{-18}$	(39)
$\text{AlF}_5^{--} \rightarrow \text{Al}^{+++} + 5\text{F}^-$	$k_5 = 4.3 \times 10^{-20}$	(39)
$\text{AlF}_6^{---} \rightarrow \text{Al}^{+++} + 6\text{F}^-$	$k_6 = 1.44 \times 10^{-20}$	(39)
$\text{HF} \rightarrow \text{H}^+ + \text{F}^-$	$k = 7.2 \times 10^{-4}$	(40)
$\text{HF} \rightarrow \text{H}^+ + \text{F}^-$	$k = 6.71 \times 10^{-4}$	(39)
$\text{F}^- + \text{HF} \rightarrow \text{HF}_2^-$	$k = 3.86$	(39)
$\text{CaF}_2 \rightarrow \text{Ca}^{++} + 2\text{F}^-$	$k = 3.4 \times 10^{-11}$ (18°)	(41)
$\text{CaF}_2 \rightarrow \text{Ca}^{++} + 2\text{F}^-$	$k = 3.95 \times 10^{-11}$ (26°)	(41)
$\text{CaF}_2 \rightarrow \text{Ca}^{++} + 2\text{F}^-$	$k = 1.7 \times 10^{-10}$	(39)
$\text{MgF}_2 \rightarrow \text{Mg}^{++} + 2\text{F}^-$	$k = 8 \times 10^{-8}$	(39)
$\text{MgF}_2 \rightarrow \text{Mg}^{++} + 2\text{F}^-$	$k = 7.1 \times 10^{-9}$ (18°)	(41)
$\text{MgF}_2 \rightarrow \text{Mg}^{++} + 2\text{F}^-$	$k = 6.4 \times 10^{-9}$ (27°)	(41)
$\text{SiF}_6^{=} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ + 6\text{F}^-$	$k = 2 \times 10^{-27}$	(39)

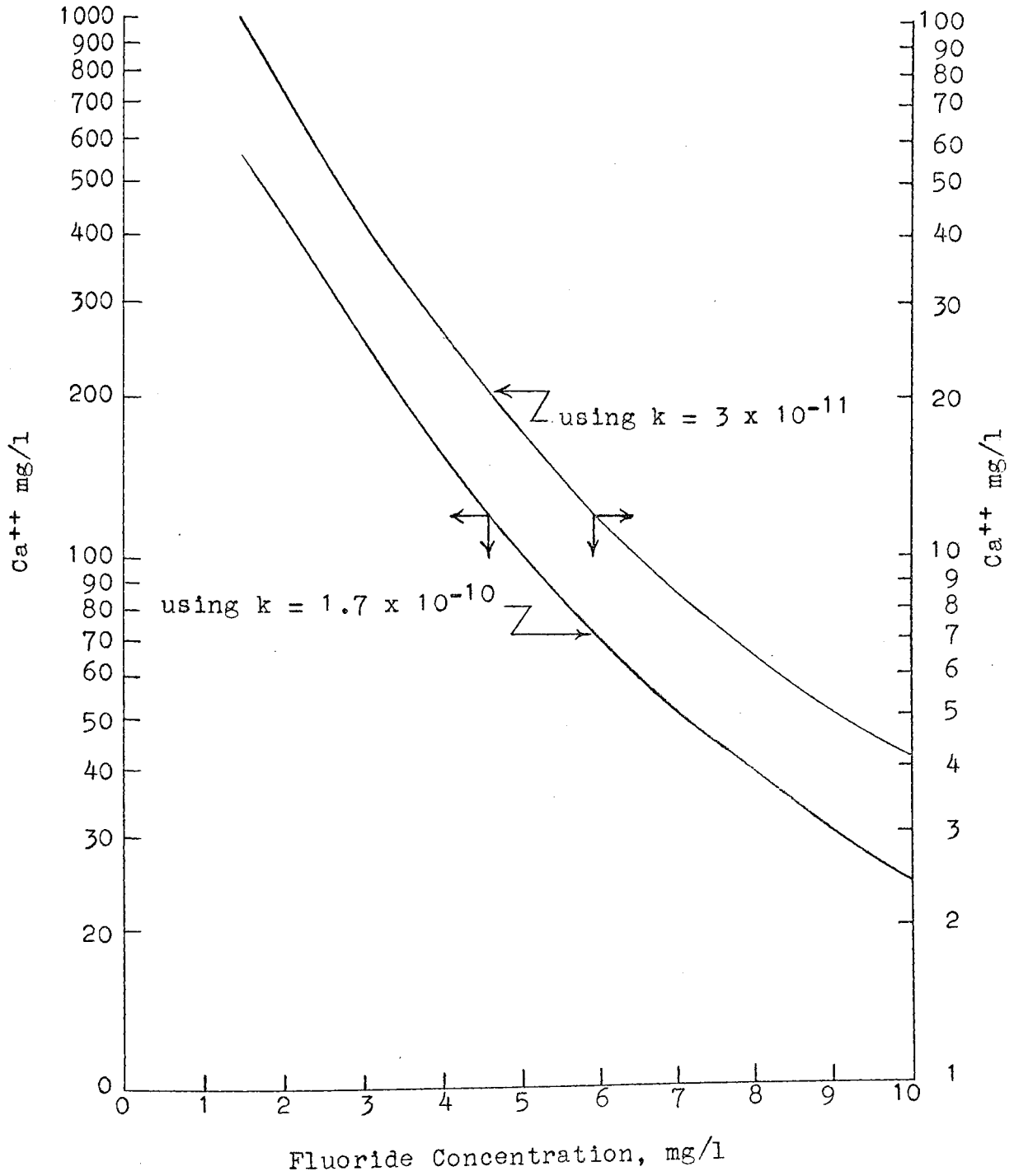


Fig. 28. CaF₂ Equilibrium Curves

APPENDIX C

THE FLUORIDE ELECTRODE AND CALIBRATION CURVES

The fluoride electrode responds to a difference in fluoride activity between an internal reference solution and the external (sample) solution. The overall response produced by a pair of internal and external reference electrodes is

$$E = E_s - \frac{2.3RT}{F} \log (F^-)$$

where E = measured potential of electrode versus reference

E_s = fixed (or standard) portion of system potential due to choice of reference electrodes and internal solutions.

$\frac{2.3RT}{F}$ = Nernst factor.

(F^-) = Fluoride ion activity in the sample solution (42).

at 25°C, the Nernst factor is 59.2 mv and at 23°C, 41.4 mv.

According to the above analysis, the readings for two fluoride concentrations a factor of 10 different should vary by the Nernst factor. This is evident in the calibration curve Fig. 29 where 1 mg/l corresponds to 100 mv and 10 mg/l to 42.5 mv. The calibration also shows that the response is linear from somewhat less than 1 mg/l F^-

to 10 mg/l F^- . Below 0.5 mg/l F^- , the curve is no longer linear.

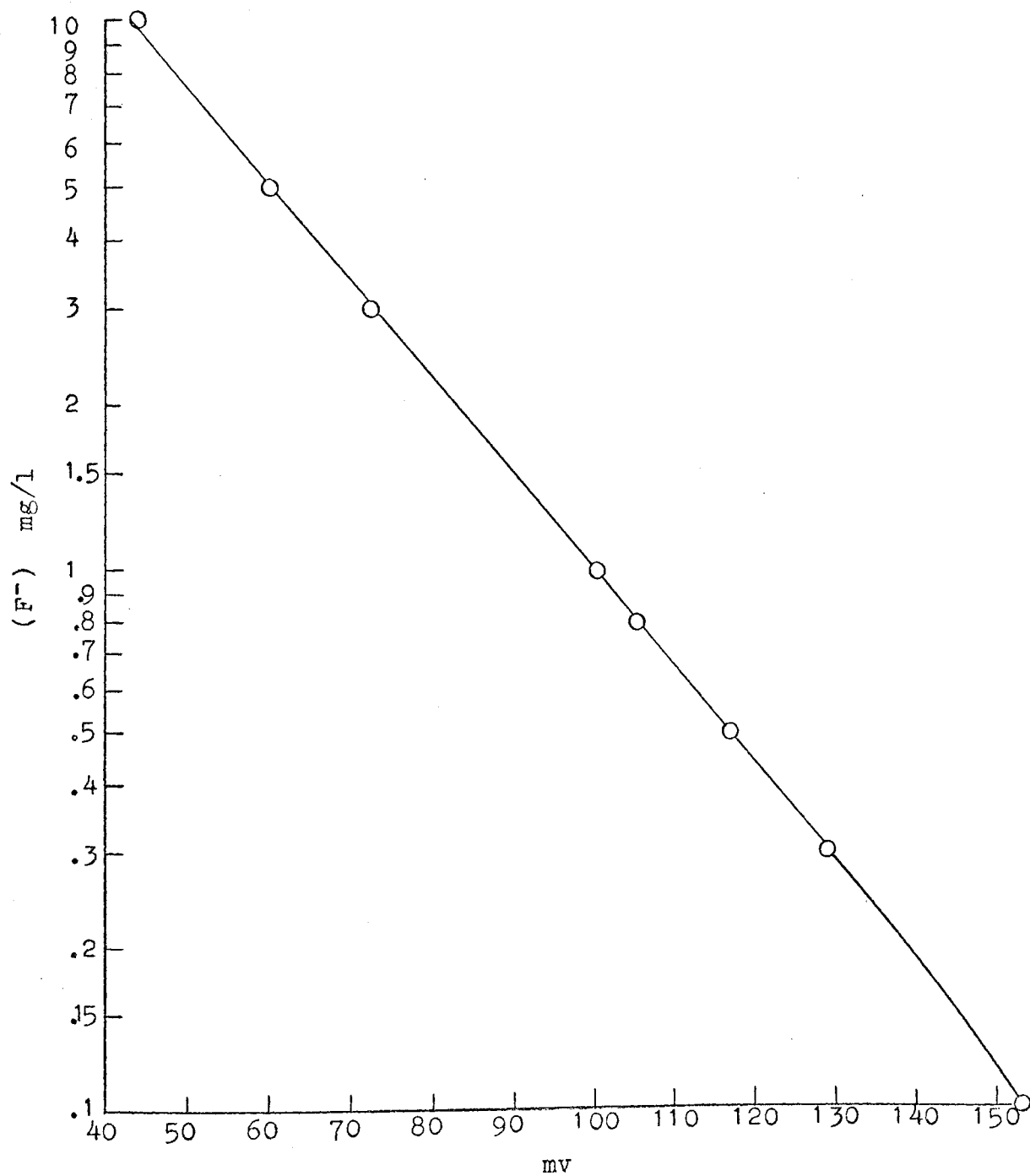


Fig. 29. Calibration Curve for Fluoride Electrode

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