

A GEOCHEMICAL INVESTIGATION OF SILICA AND FLUORIDE IN  
THE UNSATURATED ZONE OF A SEMI-ARID ENVIRONMENT

by

Randy Lynn Bassett, B.S.

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## CHAPTER I

### INTRODUCTION

#### Purpose

The United States Geological Survey is recharging potable water into the Ogallala aquifer by gravity infiltration in spreading basins. The chemistry of the water affects the permeability of the recharged formation and the utility of the water. It is essential, therefore, to be able to predict the chemical quality of the recharged water with respect to time and space. It is the purpose of this thesis to present an explanation for the changes in concentration of two constituents, silica and fluoride, observed in the recharge water as it moves through the unsaturated zone to the water table. Silica displays an anomalous solubility and fluoride behavior is of concern because of its potential as a health hazard. Because of difficulties in obtaining water samples from the unsaturated zone, little previous work has been done in this portion of the groundwater regime.

A theoretical as well as experimental approach is taken in describing this system. Using classical physico-chemical mechanisms for adsorption, anion exchange, solution, precipitation, and dispersion, a theoretical

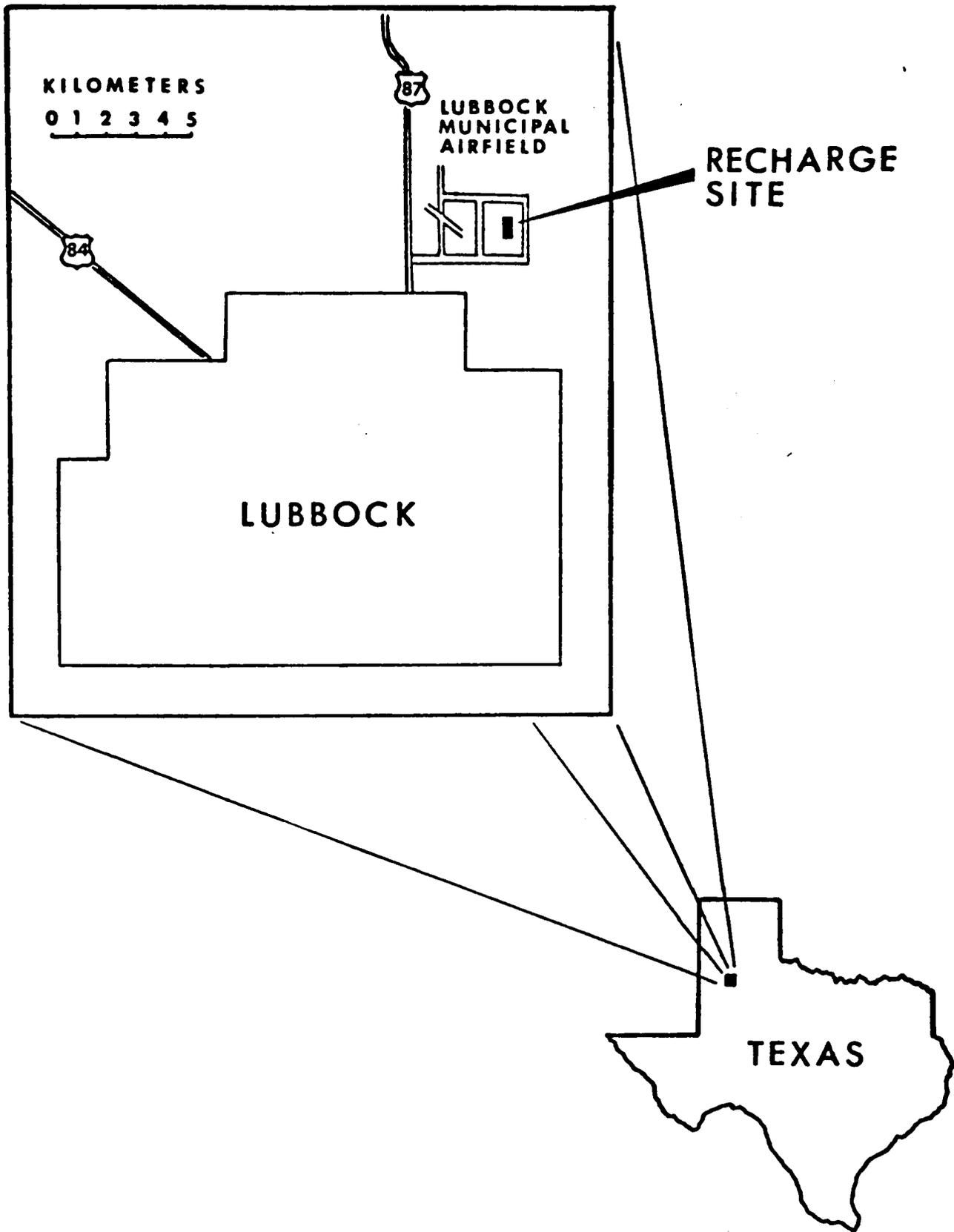


Fig. 1.--Location map.

model for the observed behavior of silica and fluoride is constructed. By experimentally determining the salient thermodynamic functions and kinetic rate relationships, the equilibrium or steady state condition is discernable, as well as the mechanisms which control the observed interactions.

The results of this investigation elucidate the state of silica and fluoride in solution in the recharge water, the source, process of removal, and equilibrium condition. Procedures will be established for evaluating the potential chemical variation of these parameters at other recharge sites.

### Regional Geography

The area of investigation is situated near the eastern edge of the Llano Estacado, the southern extension of the Great Plains physiographic province (Fig. 1). The Llano Estacado, also known as the Southern High Plains, is an area of about 75,000 square kilometers, bounded on the north by the Canadian River, on the west and east by erosional escarpments, and on the south by a gentle transition into the Edwards Plateau.

The Southern High Plains is considered essentially flat on a local scale, but regionally exhibits a gently sloping surface of 1.5 to 2.0 meters per kilometer to the southeast.

Tributaries to the Pecos River originate on the western edge of the region, and the Colorado, Red, and Brazos Rivers have headwaters on the eastern side. The only through-flowing drainage, however, is the Canadian River which separates the Southern High Plains from its northern counterpart (Reeves, 1970). The plains are relatively undissected, the only significant relief being local topographic expressions of a few meters created by sand dunes and playa lakes.

#### Climate

The Southern High Plains is a region of semi-arid climate. In general, summer temperatures are high, humidity is low, and persistent winds effect a rapid rate of evaporation, averaging over 2.0 meters of water per year (Cronin, 1964). The average annual temperature is slightly less than 16 degrees Centigrade. The month of lowest temperatures is January with the highest temperatures occurring in July. Precipitation varies from 356 mm per year in the northwest section of the Southern High Plains, to nearly 508 mm per year in the southeast portion. The Lubbock area averages about 457 mm of precipitation, most of which occurs between the months of April and September. During the calendar year of 1972, which includes the period of field investigation for this report, the

Lubbock area recorded 636 mm of precipitation (U. S. Department of Commerce, 1972). Prevailing winds are from the south and southwest averaging approximately 24 kilometers per hour 40 per cent of the time, with a slight drop in wind velocity occurring during the summer months (Johnson, 1965).

### Recharge Project

The United States Geological Survey is recharging water through a spreading basin located at the Lubbock Municipal Airport (Fig. 1). The basin was excavated in the Pleistocene and Recent eolian sediments which overlie the Pliocene Ogallala Formation. The surface consists of an Acuff soil, with a water table about 30 meters below the surface.

The soil cover was excavated to a depth of 0.3 meters at the center of the basin. This material was deposited at the edge to form a berm approximately 1 meter high, enclosing a 0.4 hectare area. The basin has a flat bottom with the berm having a slope of 1:1.

The water used to fill the recharge basin is imported from Lake Meredith, north of Amarillo, and supplied to this project by the City of Lubbock. The water typically has a total dissolved solids concentration of 1100-1200 mg/l and usually contains suspended solids in the range of 4-7 mg/l.

The water inlet to the basin is controlled by a motorized valve activated with a water-level float. Water depth is maintained at 0.6 meters 0.05 meters and is continuously monitored with a chart recorder. In addition to water level, the parameters of total inflow, water temperature, solar radiation, wind speed, infiltration rate, chemical changes in the recharge water with depth, moisture content with depth, water level in observation areas, and head pressure monitored at different levels with piezometers are also periodically recorded.

#### Method of Sample Collections and Analyses

Surface and ground waters can be sampled with little difficulty and the chemical constituencies accurately assessed. Until recently, however, it has not been possible to collect water samples from deep in the unsaturated portion of an aquifer. During this study the recharging water from a spreading basin which infiltrates the unsaturated zone is collected by means of porous ceramic cups or suction lysimeters (Wood, 1973). These cups contain a check-valve assembly which is connected to the surface by two polypropylene tubes. The system is operated by applying a vacuum to the cup, thereby inducing water to flow from the unsaturated material into the cup. Nitrogen is then supplied, under pressure, to one tube of the two-

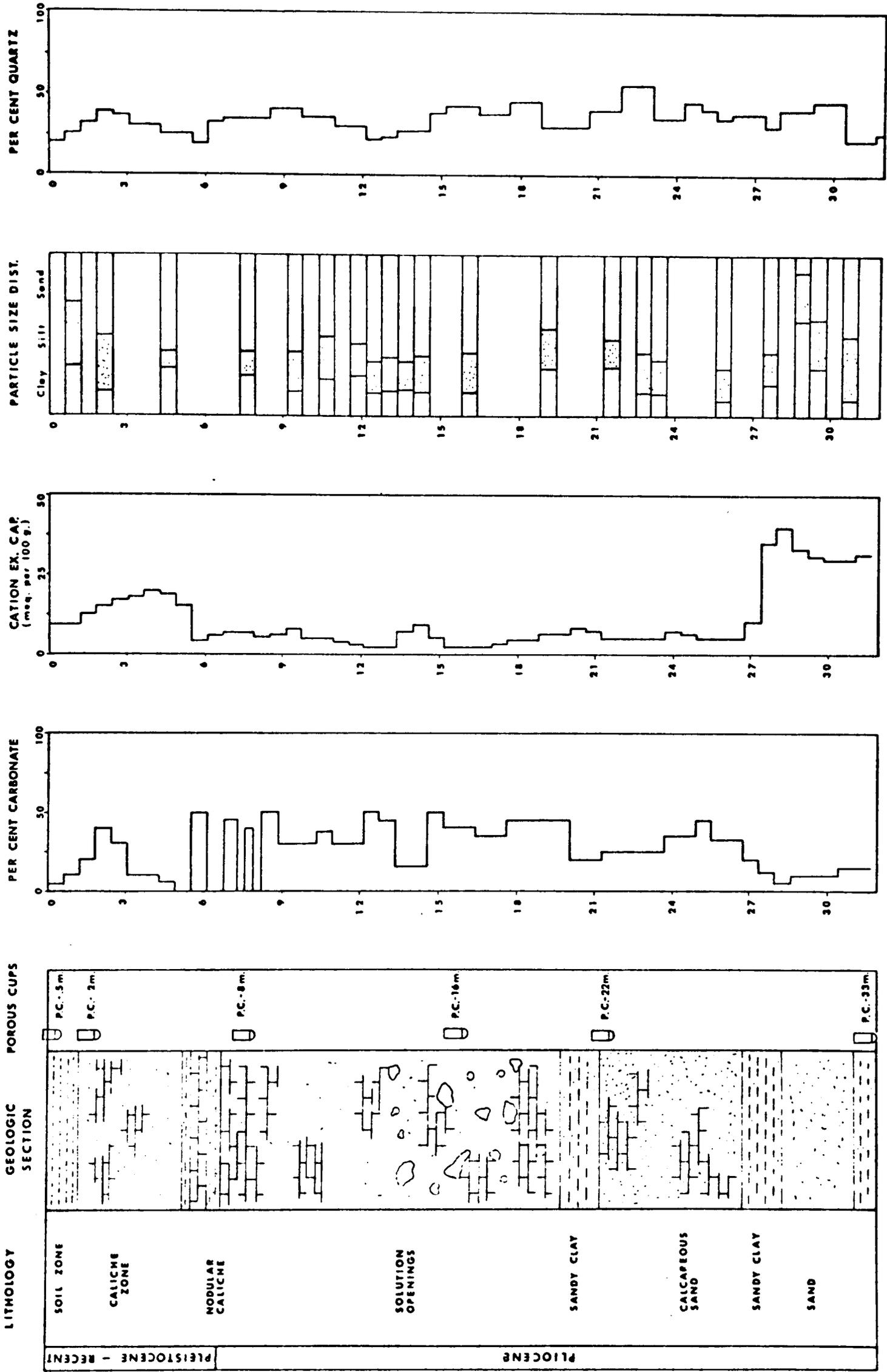
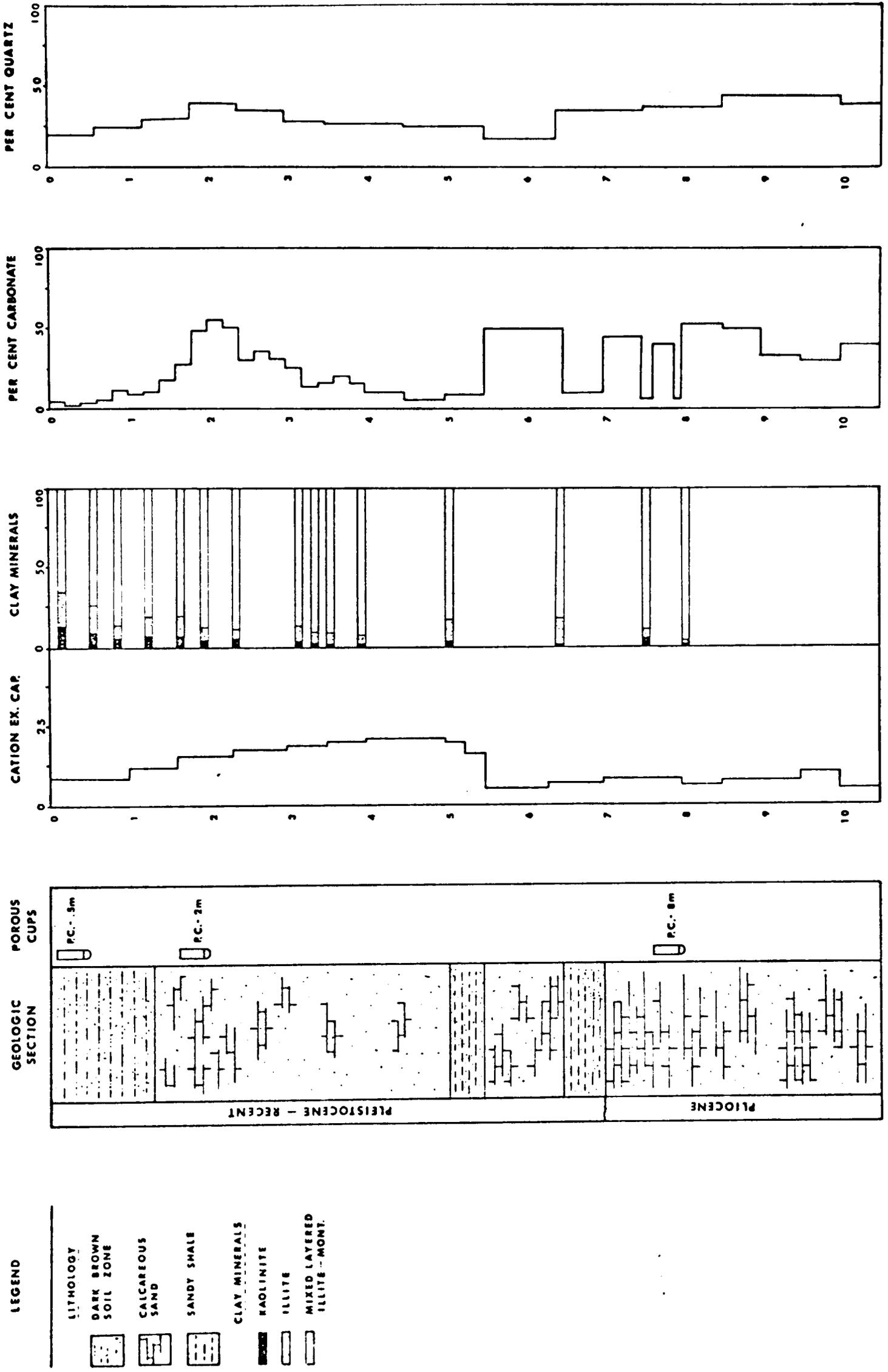


Fig. 2.--Geologic cross section.



**LEGEND**

- LITHOLOGY**
- DARK BROWN SOIL ZONE
- CALCAREOUS SAND
- SANDY SHALE
- CLAY MINERALS**
- KAOLINITE
- ILLITE
- MIXED LAYERED ILLITE-MONT.

Fig. 3.--Expanded geologic cross section.

tube system forcing the sample to the surface through the second tube. The check valve prevents pressurization of the porous cup, thus avoiding gas locking and sample loss. Porous cups used for sampling at this recharge project were buried below significant lithologic changes at 0.5, 2, 8, 16, 22, and 33 meters (Fig. 2, 3).

Samples collected from the porous cups and from the spreading basin were analyzed for pH, alkalinity, and specific conductance in a mobile laboratory adjacent to the recharge basin immediately after collection. The samples were collected in polyethylene bottles, analyzed for the unstable constituents, acidified, chloroformed, then sent to the United States Geological Survey Water Analysis Laboratory at Austin for further analysis. Analytical techniques used are those of Brown, Skougstad, and Fishman (1970).

#### Laboratory Method of Analysis

Water samples were collected regularly, and selected samples were sent to the water analysis laboratory for analysis. The remaining samples were analyzed for silica and fluoride by the author as outlined below.

For the series of laboratory experiments performed for this report, the silica concentration was determined according to a modification of the silica molybdate procedure by Boltz and Mellon (1947), Alexander (1953), Brown, Skougstad,

and Fishman (1970), for monomeric and polymeric silica. A Bausch and Lomb Spectronic 20 Spectrophotometer was used for the colorimetric detection of silica.

Fluoride activity was determined with an Orion 94-09 fluoride specific ion electrode and an Orion Ionalyzer 401 meter. The analyses of soil carbonate were performed by the United States Geological Survey Hydrologic Laboratory in Denver, Colorado, according to the method of Shapiro and Brannock (1962). Clay mineral identification was based on x-ray diffraction data obtained by the author on samples prepared according to Jackson (1958). All samples were analyzed on a Phillips Norelco X-ray Diffractometer. Both hand auger and wire-line core soil samples were used for analysis and experimentation.

### Geology and Hydrology

Most ground water used in the Southern High Plains is obtained from the Ogallala Formation of Miocene-Pliocene age. The Tertiary-Quaternary geologic history of the Southern High Plains was initially investigated by Meek and Hayden (1862) and King (1878). More recent works have been principally by Frye and Leonard (1956, 1957) and Reeves (1970, 1972). In essence, the Ogallala sediments unconformably overlies the Permian, Triassic or Cretaceous rocks (Frye and Leonard, 1957). If considered of group status, the Ogallala section is composed of the Couch

Formation, actually of late Miocene and early Pliocene age, and the Bridwell Formation which is upper Pliocene (Evans, 1949; Reeves, 1970). Reeves (1972) describes the Couch Formation as sand and gravel which is ". . . deep brown to dark red, subangular to angular, well-sorted and massive bedded." The Bridwell Formation often is distinguished from the Couch by a color contrast of reddish sand, silt, and clay (Reeves, 1972).

Zones of calcium carbonate caliche appear throughout the Ogallala section. This caliche is probably formed from infiltration of calcium carbonate and colloidal silica leached from the aggrading soil profiles and cemented to form the calcareous zones (Reeves, 1970). The top of the Ogallala section is covered by an extensive caliche "caprock" which is often several meters thick. The Ogallala section is 120 to 150 meters in thickness in the northern part of the Southern High Plains, but pinches out to the south where the Llano Estacado merges with the Edwards Plateau (Cronin, 1964).

The Ogallala sediments near the Rocky Mountains in New Mexico and Colorado are almost exclusively alluvial material (Baker, 1915) or extensions of bajada deposits. The Southern High Plains has been described as a piedmont plain of the southern Rocky Mountains which created a generally flat surface. Reeves (1972) indicates that the

surface of the piedmont is covered with tens of thousands of small depressions and a few large depressions up to 70 or 80 square kilometers, and that much of the Ogallala is eolian. The "caprock" caliche that marks the top of the Ogallala section was formed by pedogenic processes on carbonate-rich sands and loess deposits (Reeves, 1970). Cenozoic volcanic ash beds are widespread and are present in both Pliocene and Pleistocene sediments, although the Pliocene ash is often altered extensively and thus difficult to identify. Ash found in the Tule Formation of early Pleistocene age, termed the "Pearlette," has been characterized and used as a stratigraphic indicator (Frye, Swinford, and Leonard, 1948). Frye and Leonard (1957) indicate that mid-Pleistocene (Illinoian) eolian sediments called "cover sand" comprise the base on which present-day soils formed.

The "cover sands" are described as sorted, well-rounded, frosted, primarily quartz grains about 0.5 mm in size. Particle size tends to become finer toward the northeast (Carter, 1931). X-ray diffraction data by the writer indicate that potash and plagioclase feldspar comprise about 5% of the total mineralogical composition. A geologic section showing per cent carbonate, per cent quartz, cation exchange capacity, and particle size distribution is given in Figure 2.

## CHAPTER II

### SILICA STRUCTURE, SOLUBILITY, AND KINETICS

#### Structure and Solubility

"The behavior of silica in water solutions at low temperatures remains one of the most stubborn problems in geochemistry (Krauskopf, 1955)." This estimation of the state-of-the-art concerning silica research is as appropriate today as it was almost twenty years ago.

Silica displays a variety of polymorphs which tends to promote its complexity as indicated in the following classifications of low temperature forms:

1. Crystalline silica
  - a) Quartz
  - b) Tridymite
  - c) Cristobalite
2. Amorphous silica
  - a) Silica gel
  - b) Opal
  - c) Silica glass
  - d) Phytoliths
  - e) Silica skeletal remains
  - f) Metastable crystalline forms
3. Colloidal silica
  - a) Colloidal polymers

b) Silica sols

4. Silicic acid

a) Monomers

b) Oligomers

A colorimetric technique using ammonium molybdate was developed by Boltz and Melton (1947) as a quantitative measure of silica in solution. This ability to distinguish colloidal silica from the various low molecular weight oligomers in solution was an important contribution to the investigation of silica. The molybdate complexes with silicic acid to form a yellow silica molybdate solution useful for higher concentrations, or can be reduced with sulfite to an intense blue which is accurate for low concentration. Molybdate complexes with 98% of monomeric silica within 90 seconds and dimeric silicic acid within 10 minutes; thus, it is an effective technique for separating oligomers from monomeric silica.

The dissolution rate of silica is dependent upon the polymorph. It has been shown by a number of workers that quartz is the most thermodynamically stable form of silica at low temperatures; consequently, it has an extremely slow rate of dissolution. Siever (1962) demonstrated that quartz which was allowed to equilibrate in a neutral solution for three years exhibited little dissolution. However, extrapolation from higher temperature experiments indicated an

equilibrium value of 4.9 mg/l  $\text{SiO}_2$ .

The solubility of quartz mechanically tumbled in a water solution at various temperatures and pressures was studied by Morey, Fournier, and Rowe (1962). Tumbling and consequent abrasion increased the rate of solution; however, the solution equilibrated at a concentration near 6 mg/l  $\text{SiO}_2$ . This experiment indicated the rate of solution was much faster in this environment, but the equilibrium value was the same as in a quiescent environment. Since that time many workers have verified the equilibrium value of quartz in a water solution of neutral pH, as being between 6 and 10 mg/l  $\text{SiO}_2$ . The rate of dissolution is dependent on the surface area exposed but is still extremely slow (Krauskopf, 1967; Polzer, 1967; Stöber, 1967).

The solubility of amorphous forms of silica has been the subject of many detailed investigations (Alexander, Heston, and Iler, 1954; Holt and King, 1955; Greenberg and Price, 1957; Morey, Fournier, and Rowe, 1964; Siever, 1962; Stöber, 1967). Amorphous polymorphs as defined by Siever (1962) include varieties of silica gel, silica glass, opal, skeletal remains of silica secreting organisms, and the metastable forms of tridymite and cristobalite since they are not thermodynamically stable at standard temperatures and pressures.

These investigations seem to agree that the various

forms of amorphous silica have definite solubility values which differ only slightly from one type to another over the range of 115 to 140 mg/l  $\text{SiO}_2$ . Equilibration has been approached both by dissolution and supersaturation. The rate of dissolution is faster for amorphous silica (Fig. 4) but still requires several months for equilibration (Morey, Fournier, Rowe, 1964). Silica gels, glasses, opals, and diatomaceous materials all seem to follow this solubility scheme which is independent of pH from pH 2 to pH 9 (Siever, 1962). Metastable silica such as tridymite and cristobalite have equilibrium concentrations reported between amorphous silica and quartz (Morey, Fournier, and Rowe, 1962).

Polymeric or colloidal silica was defined by Iler (1955) as ". . . a dispersion of silica in a liquid medium in which the particle size of the silica is within the colloidal range." The range of colloidal sized particles is generally accepted as the fraction of particles with diameters from  $10^{-3}$  to  $10^{-6}$  mm, which represents the size of particles in suspensions and true solutions.

Silica colloids vary in particle size and degree of hydration. Colloids are high molecular weight polymeric chains of silicic acid which are stable indefinitely in suspension as a sol. Sols will coagulate to form a silica gel when mixed with relatively high concentrations of

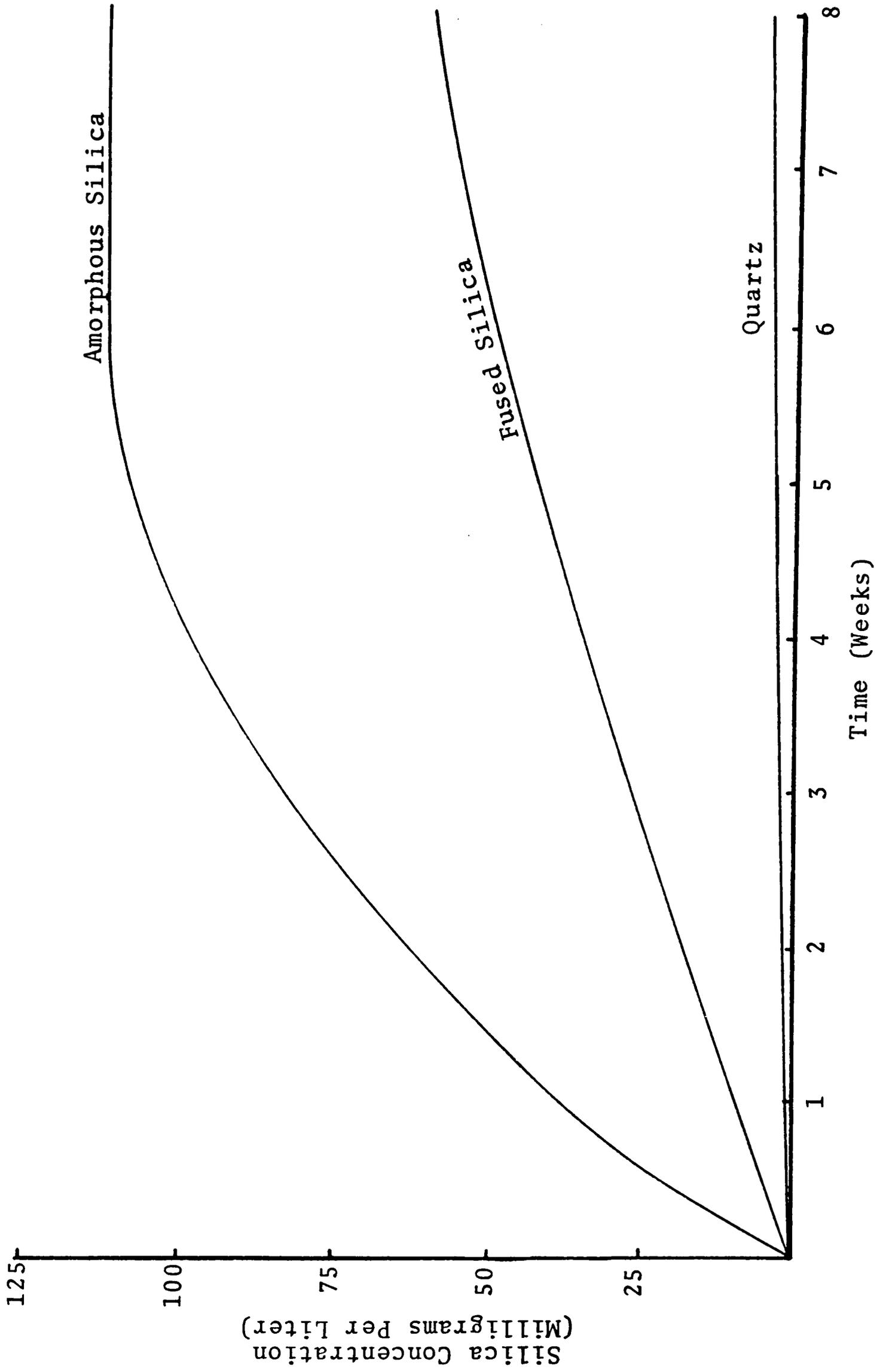


Fig. 4.--Solution Rates for silica polymorphs.

electrolytes or supersaturated with several hundred milligrams silica per liter (Iler, 1955; Krauskopf, 1967).

Silica is in true solution only as low molecular weight silicic acid molecules called oligomers. Oligomers contain from 1 to 6 molecules of monosilic acid, which is a silicon atom coordinated with four hydroxyl groups (Fig. 5).

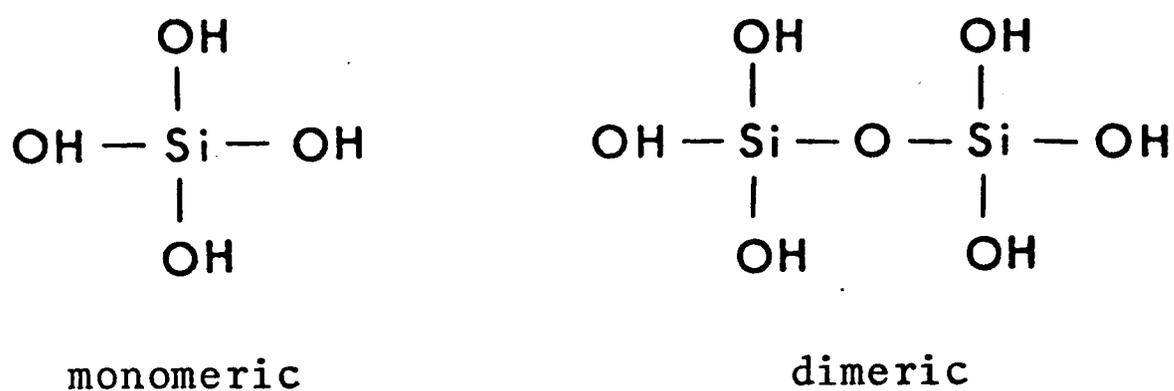


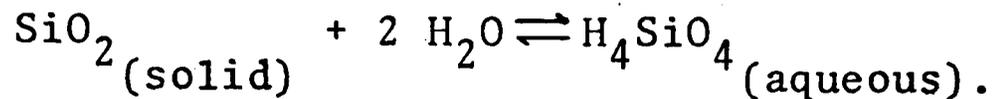
Fig. 5--Silicic acid structure.

Silicic acid is a weak acid analogous to carbonic acid, but with an ionization constant about  $1 \times 10^{-3}$  of that for carbonic acid (Krauskopf, 1967).

$$K_1 = \frac{[\text{H}^+] [\text{H}_3 \text{SiO}_4^-]}{[\text{H}_4 \text{SiO}_4]} = 10^{-9.91}$$

An earlier work by Sillen and Martell (1964) listed the

first dissociation step as half completed between pH 9.41 and pH 9.91. A general equilibrium equation for the hydrolysis of silica in an aqueous solution to form ortho-silicic acid may be written as:



There is no appreciable dissolution of silicic acid in an aqueous solution at neutral pH so the equilibrium constant may be defined as simply the concentration of monosilicic acid:

$$K_{\text{eq}} = \frac{[\text{H}_4\text{SiO}_4]_{\text{aq}}}{[\text{SiO}_2]_{\text{s}}} = [\text{H}_4\text{SiO}_4]_{\text{aq}}.$$

Even though the equilibrium concentration and dissolution rates vary widely between the various forms of silica they can be grouped into two broad categories of quartz and amorphous. Polzer (1967) calculated the following equilibrium values at 25°C from previously published work:

Quartz  $K_{\text{eq}} = 1 \times 10^{-4}$  moles/liter

Amorphous  $K_{\text{eq}} = 2 \times 10^{-3}$  moles/liter

silica

### Dissolution Kinetics

The concentration of silica in the Canadian River water used in the recharge basin, averaged 0.4 mg/l  $\text{SiO}_2$  from April to December, 1972 (Fig. 6). Concentration of silica in the recharged water, observed at a depth of 0.5 m below the surface, showed an initial concentration of 8.3 mg/l  $\text{SiO}_2$  and within 20 hours reached a peak concentration of 35 mg/l  $\text{SiO}_2$ . From this high value the concentration steadily decreased until the recharged water had the same concentration as the input about 45 days later (Fig. 6). In all cases the silicic acid was monomeric; the color developed within 2 minutes. Boiling with NaOH did not produce any increase in total silica concentration. This phenomenon of initial rapid dissolution and subsequent slow decline in concentration was observed at all the depths at which samples were collected. It can also be seen that the concentration was cumulative. Thus, each water sample had a greater concentration of silica than the water sample for the cup above, up to a maximum of 110 mg/l  $\text{SiO}_2$  (Fig. 6). The problem can be simply stated: what is the source of this silica? How does it enter into solution? What is the equilibrium value? How can the concentration be predicted with respect to time and depth?

Based on previously discussed solubility rates, (Fig. 4), it seems somewhat unlikely that the observed rapid

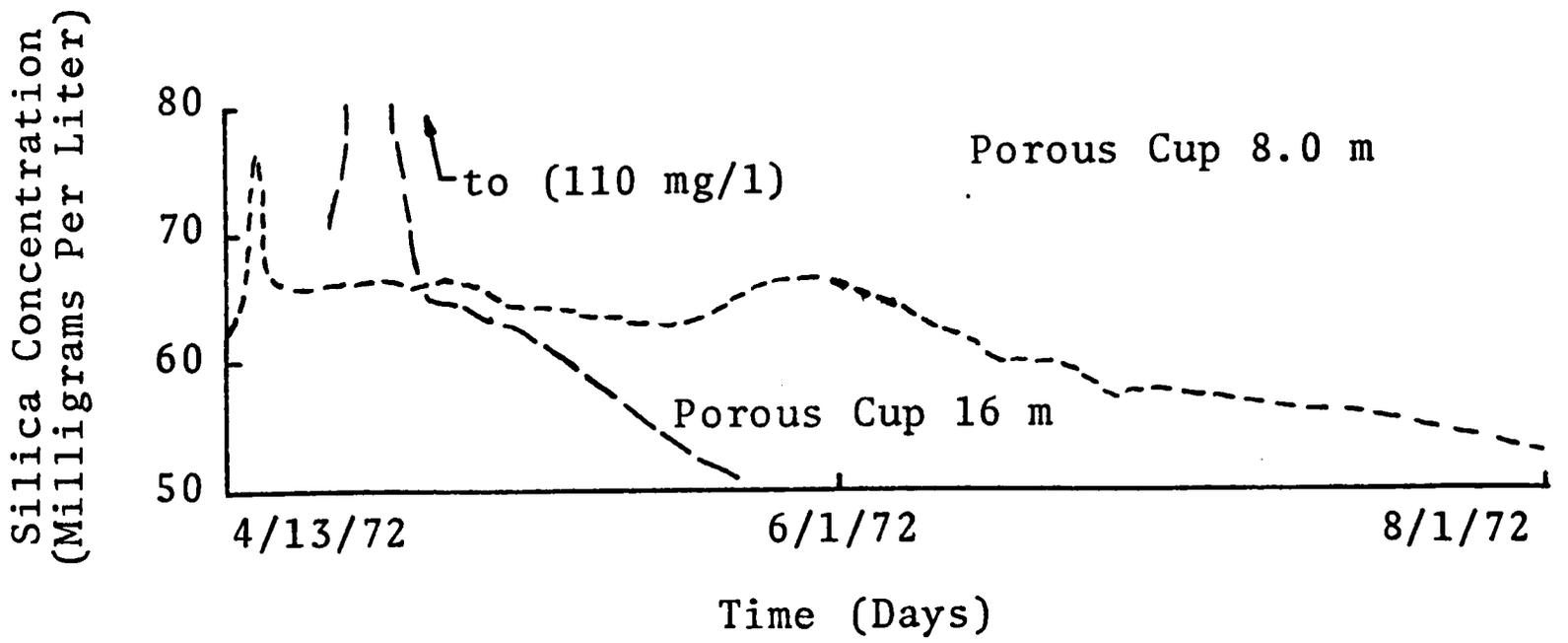
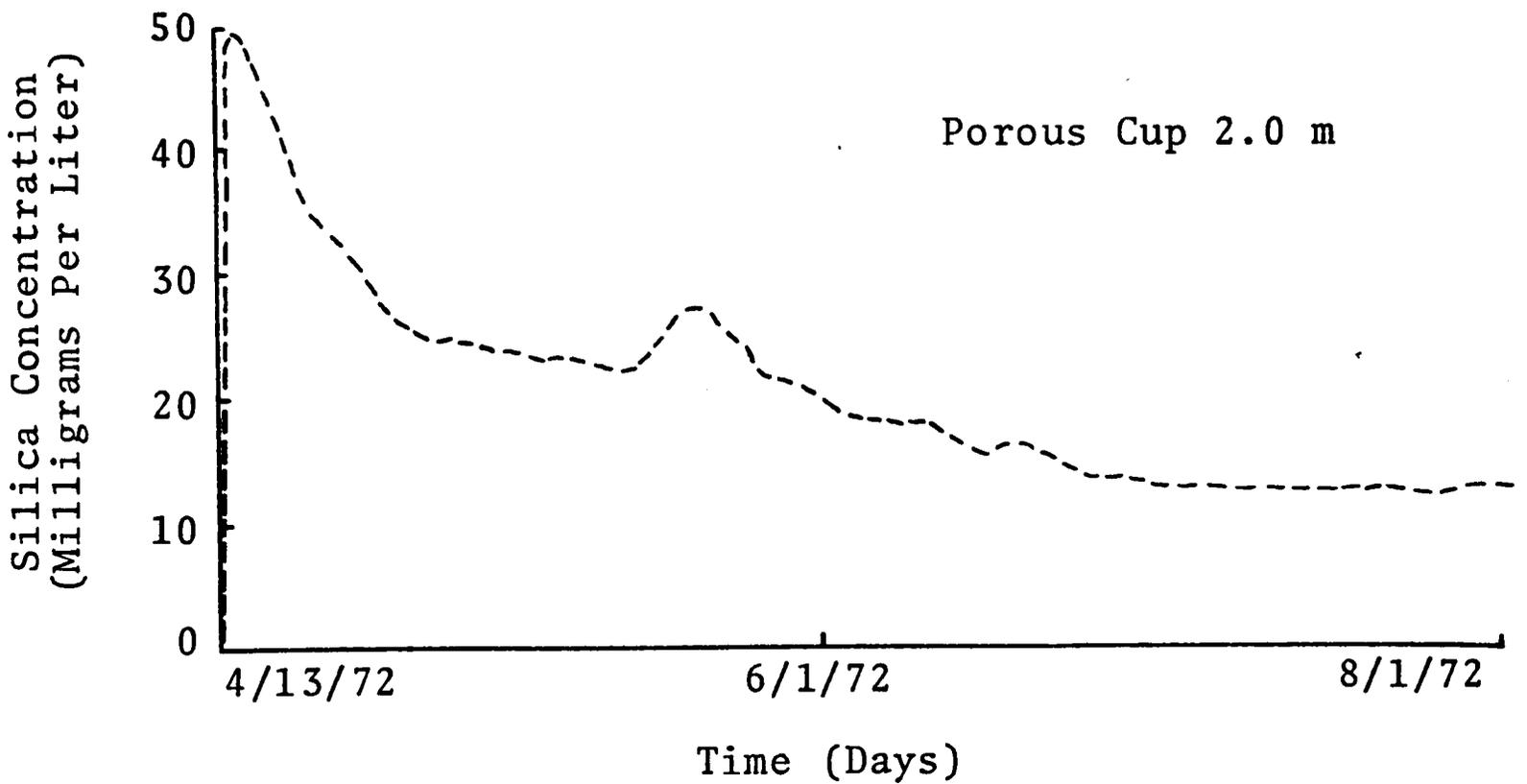
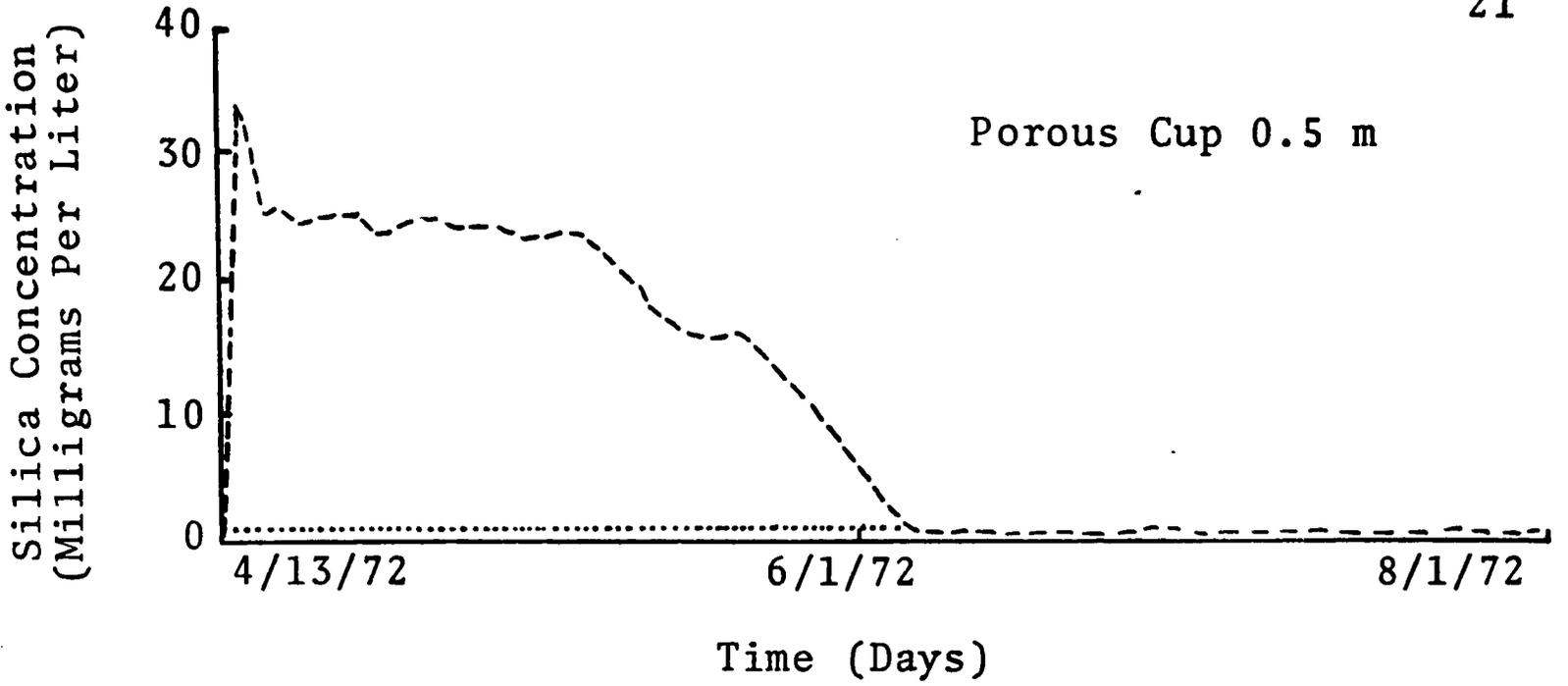


Fig. 6.--Porous cup data for silica concentration.

increase in silica concentration evidenced in the sample intervals could be completely attributed to the dissolution of quartz, amorphous, or colloidal silica. Clelland and Ritchie (1952) observed an initial rapid increase in silica concentration when quartz was equilibrated with water and attributed this to surface imperfections. Holt and King (1955) demonstrated that surface imperfections were not responsible for the phenomenon, and proposed an adsorbed monolayer of monomeric silicic acid that was establishing an equilibrium between the silica powder and water. They removed the "adsorbed layer" with sodium hydroxide, then reestablished equilibrium from a supersaturated solution.

It was also shown by Holt and King (1955) using radioactive  $^{31}\text{Si}$  that the adsorption equilibrium was dynamic, since labeled silica in solution exchanged with the adsorbed silica. Weyl and Hauser (1951) contended that adsorption or condensation was the result of a tendency of silicon to expand its outer shell of electrons to 12 by coordination with two hydroxyl groups or with two water molecules. Iler (1955) also supports that contention and postulates that monomeric silica polymerizes in this fashion (Fig. 7) creating a temporary or apparent coordination number of 6.

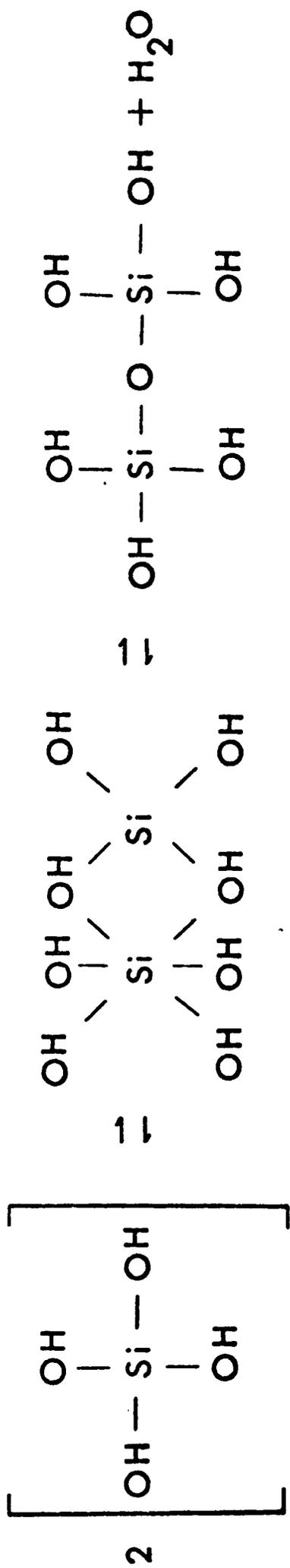


Fig. 7.--Silica Polymerization.

Polzer (1967) pointed out that even though the existence of ions in 6 coordination has not been confirmed, it is well known that six-fold coordination with fluoride does exist  $(\text{SiF}_6)^{-2}$ . When the  $\text{H}^+$  ion penetrates the electron cloud of an  $\text{O}^{-2}$  ion the ionic diameter of the resultant  $\text{OH}^-$  is reduced to approximately that of fluoride. The importance of this observation is that the mechanism of attachment of monomeric silica could be an expansion from four to six-fold coordination. This expansion incorporates the hydroxyls that are on the hydrated silica surface of crystalline or amorphous silica.

If the silica observed in the recharge water is from desorption of monomeric silicic acid on quartz grain surfaces, then the solubility rate will be rapid compared to that of amorphous silica or quartz. The adsorbed layer should also be completely extractable; after which, any concentration of silica observable in the solvent would be a result of dissolution and hydrolysis of the silicate structure.

A kinetic model representing the hydrolysis of silica was proposed by Stöber (1967). He postulated that the dissolution of silica was not simply a first order rate mechanism, but rather the process passed through an adsorption phase. Stöber suggests that when the initially

adsorbed monomeric silica is removed from silica surfaces, the equilibrium is maintained by means of a four step process. First the Si-O-Si bonds are broken at the silica surface and a hydrated silica monomer is formed. This monomer is then adsorbed onto the surface before being released into the solvent. The third step is readsorption of silicic acid from solution, back onto the silica surface. The last step is condensation or precipitation of the readsorbed silica into some unextractable phase continuous with the silicate structure. The following four assumptions are used in Stöber's model:

1. The adsorbed phase can be represented by the Langmuir isotherm

$$N_{\text{ads}} = \frac{N_0 bc}{1 + bc}$$

$N_{\text{ads}}$  = Surface concentration of silicic acid

$N_0$  = Monolayer concentration

$c$  = Silica solution concentration

$b$  = Adsorption constant.

2. Hydrolysis occurs on sites not occupied by adsorbed silica.
3. The adsorption equilibrium is established rapidly, relative to the other processes.

4. Precipitation occurs for adsorbed molecules only.

The integrated equation used for this model estimates the time it takes to obtain various concentration levels

$$t = \frac{c_e}{k} \left( \frac{b \ln[1+bc]}{1+bc_e} - \frac{Vbc}{n_o F} - \frac{bn_o F + V[1+bc_e]^2}{n_o F[1+bc_e]} \ln \left( \frac{1-c}{c_e} \right) \right)$$

where

- $c_e$  = Saturated concentration of silicic acid  
 $c$  = Silicic acid concentration at time  $t$   
 $b$  = Adsorption constant  
 $k$  = Rate constant for surface reactions  
 $F$  = Total silica surface area  
 $t$  = Time (hours)  
 $V$  = Solvent volume  
 $n_o$  = Silica adsorption sites.

By using different particle sizes, Stöber was able to show that the rate of dissolution was dependent on surface area. He also noted that the equilibrium value for quartz was about 12 mg/l which is higher than that obtained by other workers (Seiver, 1962; Morey, Fournier, and Rowe, 1962). Stöber attributes the phenomenon to the catalytic

effect of the sodium chloride solution used.

### Dissolution Experiment

The following experiment was conducted on samples of material from the recharge site to determine (1) the rate of solution of the initially "adsorbed" silica, (2) if the soil samples reacted differently when the "adsorbed" surface layer was removed and (3) if this different behavior could be modeled according to Stöber's proposed mechanism. The soil used for this analysis was removed from an area immediately adjacent to the recharge basin by hand auger. The sample collected at a depth of 1.8 m was taken from a sandy zone (Fig. 2) which would correspond to a point between the sampling depths at 0.5 m and 2 m.

Three samples A, B, and C, each sufficient to yield 25 grams of material, were treated as follows: Sample A was washed three times with 0.5 N NaOH, then three times with 0.1 N NaCl, to remove any adsorbed silica, and finally neutralized to a pH of 7.5 with HCl. This washing technique or a similar one has been used by many workers to remove adsorbed silica (Stöber, 1967; Morey, Fournier, and Rowe, 1964). The material used in sample B was sieved to remove particles less than 40 microns in diameter, then

washed as above. The material used in sample C was air dried only.

Using data obtained from these experiments and information given by Stöber, the following values were determined:

$$c_e = 12 \text{ mg/ml}$$

$$c = \text{Increments from 0 to 12 mg/ml}$$

$$b = \text{Langmuir adsorption constant } 0.7 \text{ ml/mg}$$

$$k = 1.7^{-1/24} \text{ hours}$$

$$F = 0.5999 \text{ m}^2/25\text{g}$$

$$t = \text{Time (hours)}$$

$$V = 125 \text{ ml}$$

$$n_o = 10 \text{ moles/m}^2 \text{ for silica adsorption sites.}$$

The value for surface area was calculated according to Herdan (1960). A 50 gm sample of the same material used in the test was sieved with standard screens incremented approximately every 25 microns from 1000 microns to 50 microns in particle diameter.

A hydrometer test was conducted on the clay and silt size particles to obtain percent weight according to Bouyoucos (1951). Surface area for clay-sized silica particles was based on x-ray diffraction analyses which showed 95% of this size fraction was clay or carbonate and 5% was quartz grains.

The results of the experiment are illustrated in Fig. 8. The changes in concentration of silica in the three samples A, B, and C are plotted as a function of time. In sample C, the adsorbed silica is still present and desorbs very rapidly, reaching equilibrium within 12 hours (Fig. 8). Both samples A and B have been washed with hydroxide to remove the adsorbed layer; so, the rate of change of concentration with time represents simply the hydrolysis of the silicate structure. Using Stöber's model the theoretical dissolution rate for quartz with a surface area which is the same as that calculated for samples A and B is also plotted in Fig. 8. As can be seen from the graph, the theoretical rate and concentration agrees quite well with the rates actually observed in A and B. This experiment shows that the simple dissolution of silica from quartz does not explain the observed silica concentration in the recharge water, but the "adsorbed" silica possibly could.

#### Enthalpy of Monosilicic Acid

An adsorption mechanism involves energy for attachment and removal. Adsorption must be exothermic; therefore, raising the temperature should increase desorption (Trapnell, 1955).

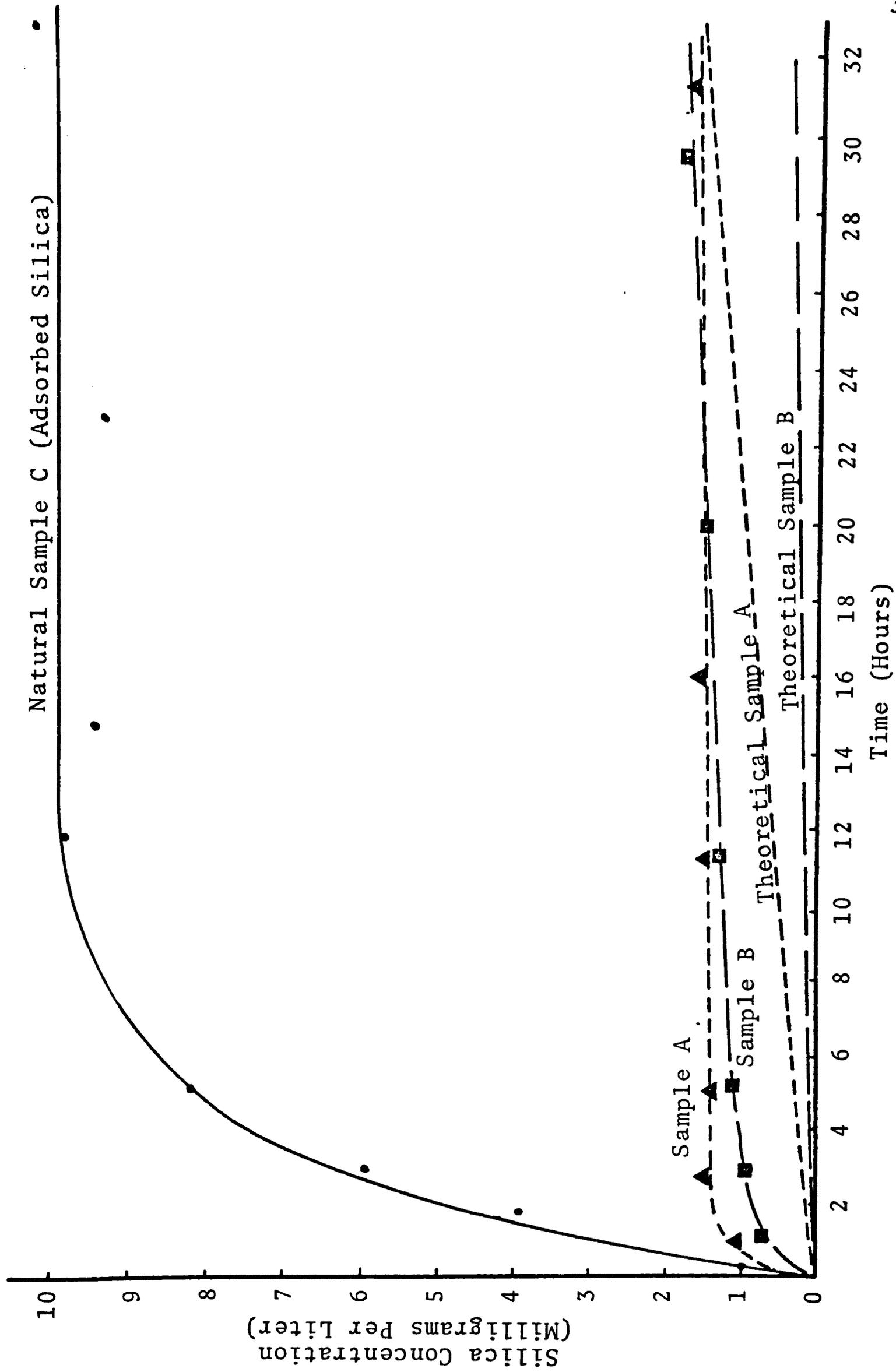


Fig. 8.--Dissolution rates of silica in soil samples.

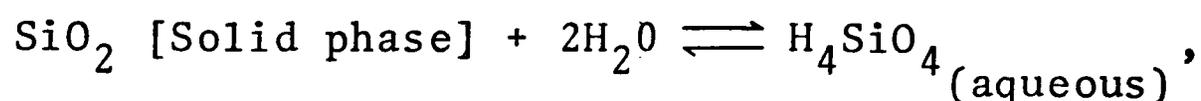
Gifford and Frugoli (1964) concurred with Greenberg (1956) that this "adsorbed" layer or "solid monosilicic" acid attached in some fashion, has a definite heat of solution ( $\Delta H$ ). They determined this value by using the van't Hoff equation in the form written below:

$$\log K_{eq} = \left( \frac{-\Delta H}{2.303 R} \right) \left( \frac{1}{T} \right) + C$$

where

- K = Equilibrium constant
- R = Gas constant
- T = Temperature (degrees Kelvin)
- $\Delta H$  = Heat of formation of silicic acid
- C = Constant of integration.

If the equilibrium equation were written as:



then the equilibrium constant is simply the concentration

$$K_{eq} = [\text{H}_4\text{SiO}_4]_{aq}$$

of monosilicic acid in solution when equilibrium has been attained.

Greenberg (1956) was able to calculate a  $\Delta H$  value from data given in the literature for this surface phase of silica. Gifford and Frugoli (1964) confirmed Greenberg's  $\Delta H$  value by experimental determinations. The values for  $\Delta H$  given by these workers are listed below (Table 1) for quartz, amorphous silica, and monosilicic acid.

TABLE 1  
ENTHALPY VALUES FOR SILICA POLYMORPHS

<u>Polymorph</u>	<u><math>\Delta H</math> Kcal/M</u>	<u>Worker</u>
Quartz	+7.34	Greenberg (1956)
Amorphous silica	+2.65	Greenberg (1956)
Monosilicic acid	+4.50	Greenberg (1956)
Monosilicic acid	+4.0-4.2	Gifford and Frugoli (1964)

If the rapidly soluble silica observed both in the recharge site samples (Fig. 6) and in experimental work (Fig. 8) is from desorption of a surface phase of monosilicic acid, then it should be possible to determine a value for  $K_{eq}$  at different temperatures and then calculate the corresponding  $\Delta H$ .

The following experiment was conducted to determine the equilibrium concentration of monomeric silica at three temperatures with samples representing three different particle sizes.

Representative material obtained from the recharge area was mechanically separated into three size ranges: less than 125 microns, 125 microns to 250 microns, and 500 microns to 1000 microns in diameters. Nine 20 gram samples, three from each size range, were placed in 100 ml of 0.1 N NaCl solution. The pH of the slurry was adjusted to 7.5 with HCl and the bottles were immediately stoppered and allowed to equilibrate at 3 different temperatures: 1°C, 22°C, and 50°C.

The changes in concentration were monitored regularly and are shown in Figures 9, 10, and 11. In all three samples an initial rapid increase in concentration is observed which is somewhat accelerated with increased temperature. Equilibrium values for the three size fractions at corresponding temperatures are similar and stable for at least a week. The equilibrium concentrations or  $K_{eq}$  values are tabulated on the following page (Table 2) from data used in preparing Figures 9, 10, and 11.

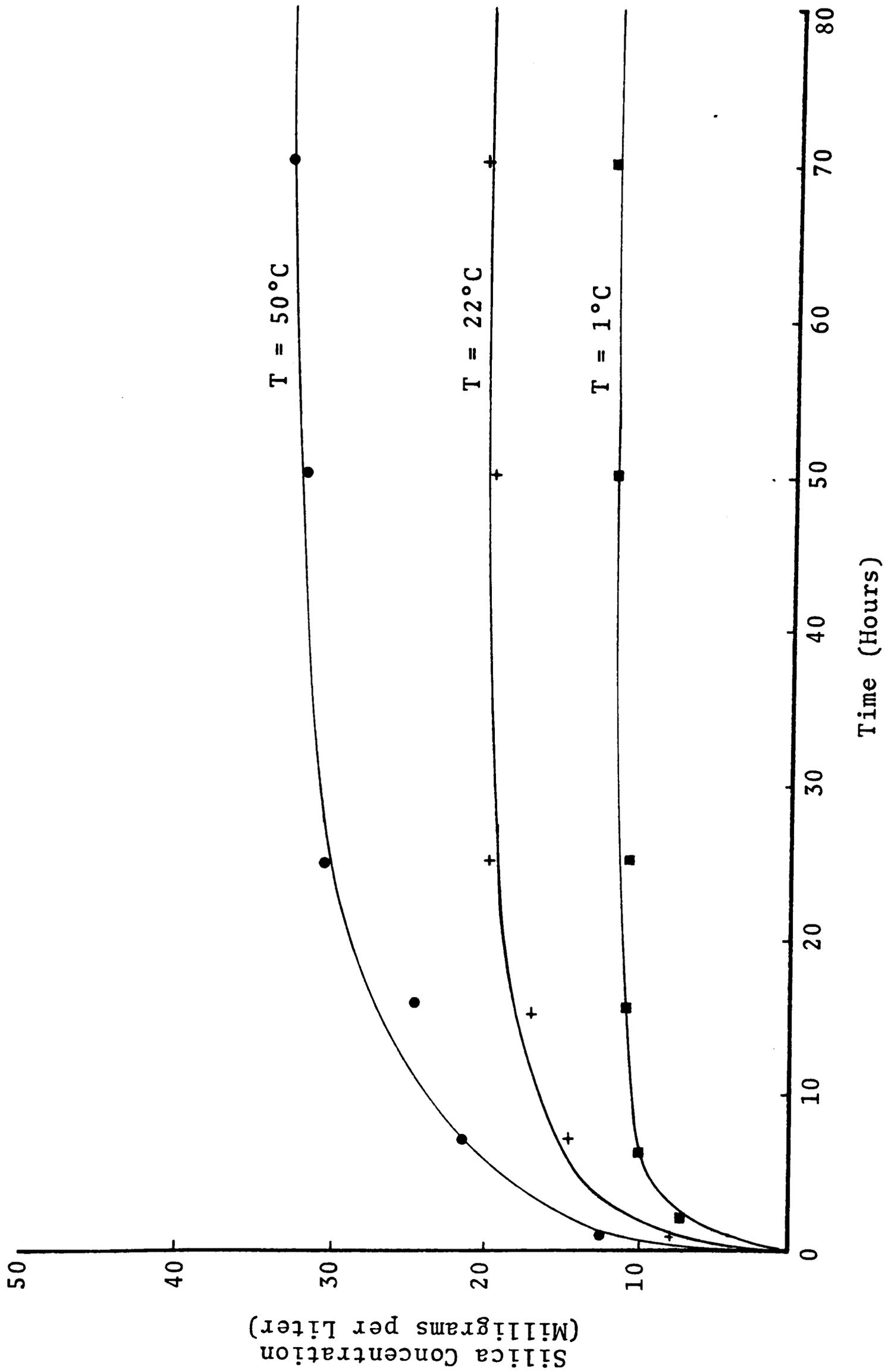


Fig. 9.--Silica equilibrium concentrations for 125 micron sample.

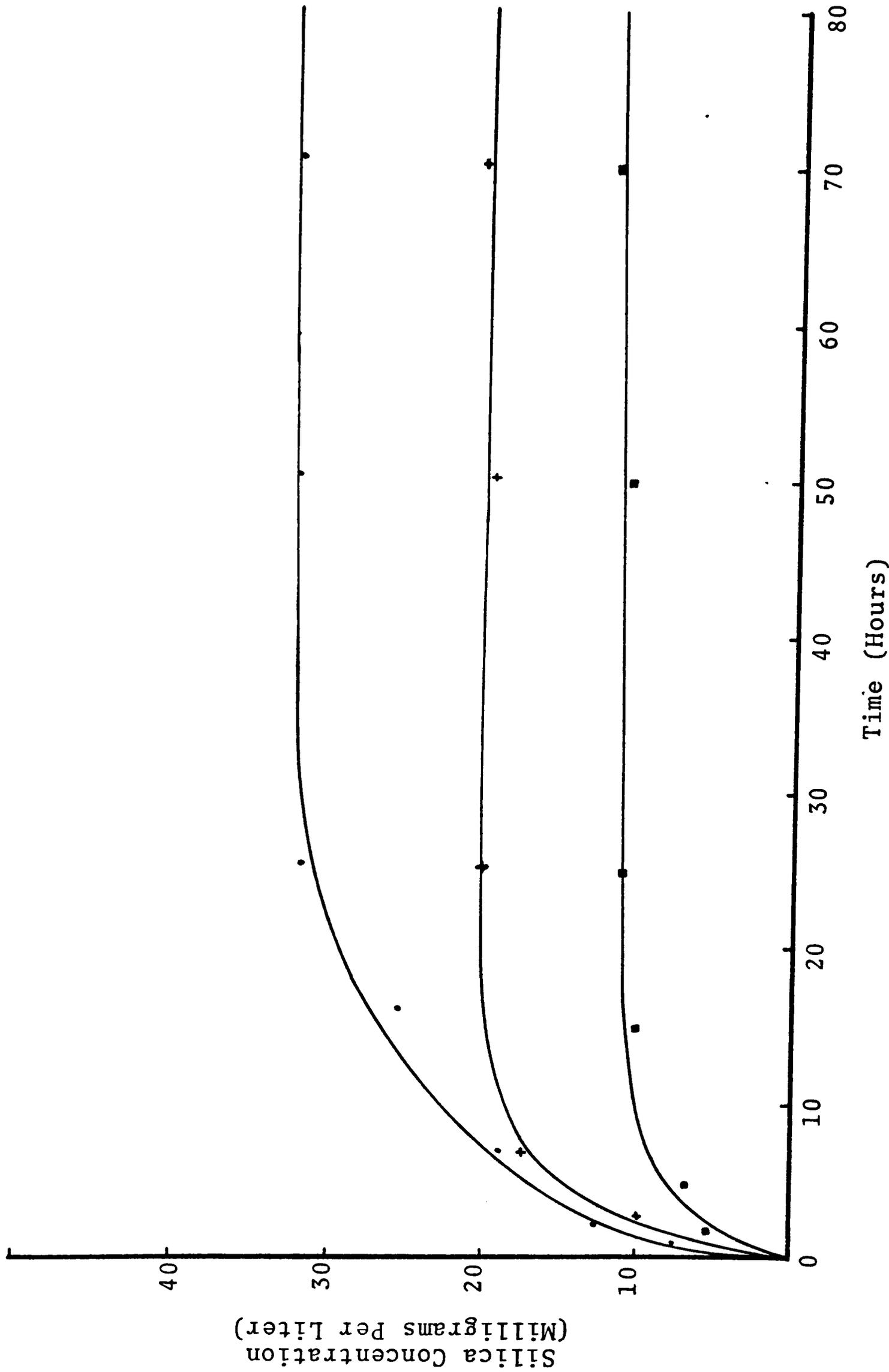


Fig. 10.--Silica equilibrium concentrations for 125 micron to 250 micron sample. 35

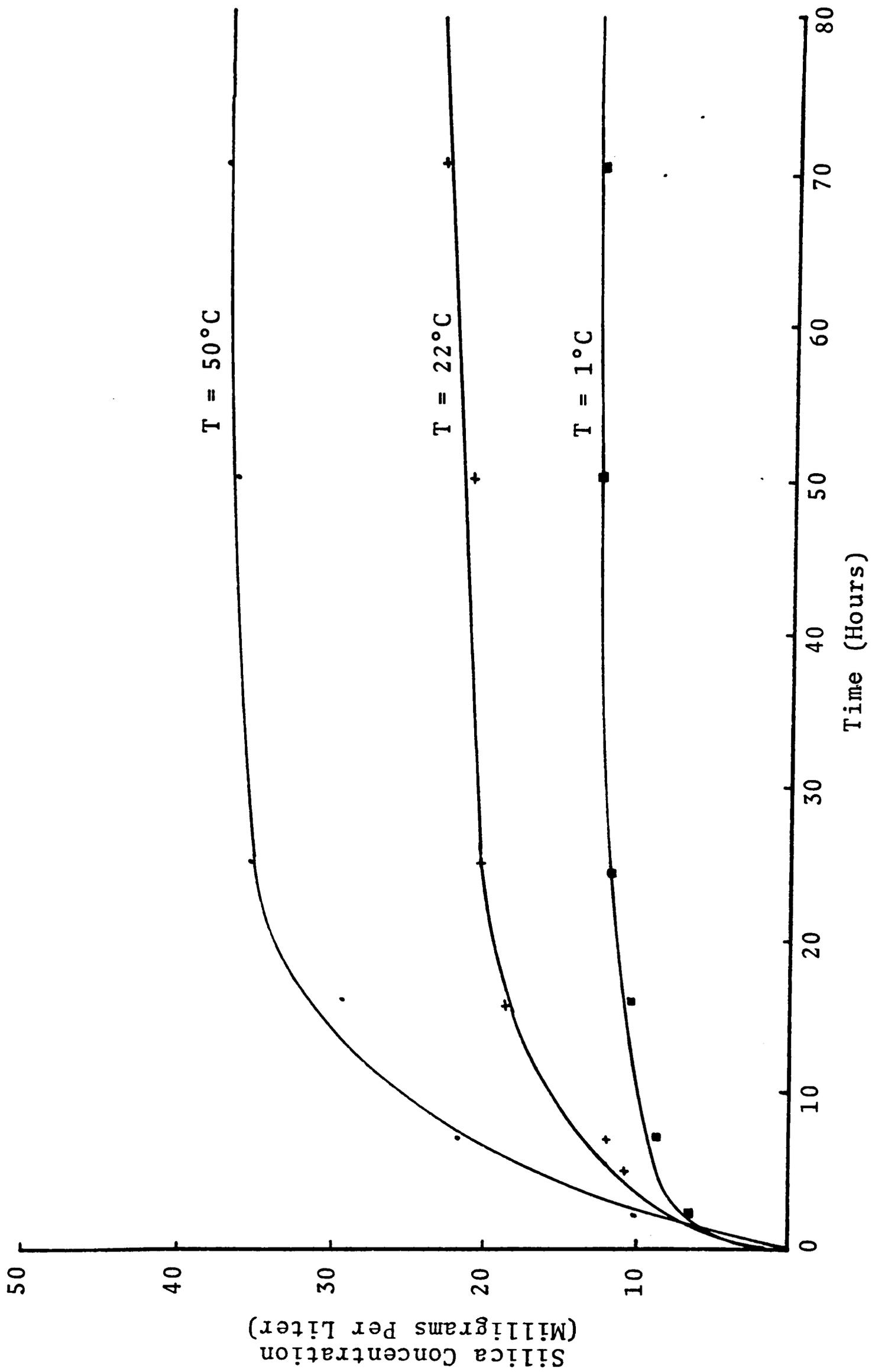


Fig. 11.--Silica equilibrium concentrations for 500 micron to 1000 micron sample. 36

TABLE 2  
SILICA CONCENTRATIONS FOR VARIOUS SIZE FRACTIONS

<u>Size Fraction</u>	<u><math>K_{eqT = 1^{\circ}C}</math></u>	<u><math>K_{eqT = 22^{\circ}C}</math></u>	<u><math>K_{eqT = 50^{\circ}C}</math></u>
less than 125 $\mu$	11.5	21.5	33
125 $\mu$ to 250 $\mu$	11.5	20.5	32.5
500 $\mu$ to 1000 $\mu$	12.0	21.5	33

Knowing the  $K_{eq}$ , the  $\Delta H$  value can be calculated using the van't Hoff equation in the following way: if the negative logarithm of the silicic acid concentration ( $-\log K_{eq}$ ) is plotted against the reciprocal of the absolute temperature, the slope of the resultant line is equal to  $\frac{-\Delta H}{2.303R}$  (Fig. 12). The heat of solution then is

$$\Delta H = - [\text{slope}] \times [2.303R].$$

The calculated heats of solution are given in Table 3 for the three size fractions.

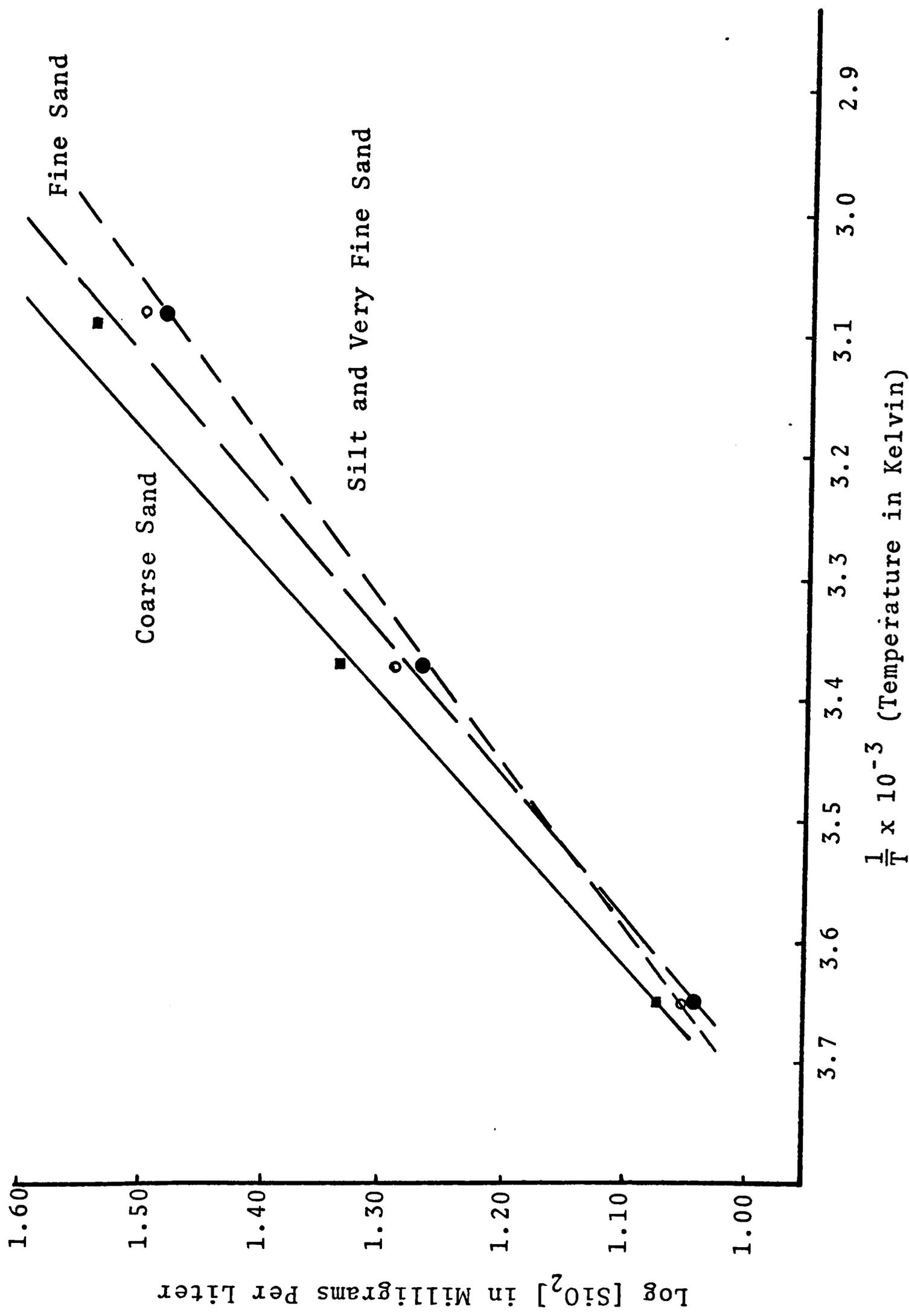


Fig. 12.--Silica concentration according to the van't Hoff equation.

TABLE 3  
ENTHALPY VALUES FOR VARIOUS  
SIZE FRACTIONS

<u>Size Fraction</u>	<u><math>\Delta H</math> Kcal/Mole</u>
>125 $\mu$	+3.66
125 $\mu$ - 250 $\mu$	+4.00
500 $\mu$ 1000 $\mu$	+4.26

The values for heat of formation are close to those determined by other workers for monosilicic acid (Table 2). The silica concentration was temperature dependent as predicted by Trapnell (1955) and in all cases was present as the monomeric form of silicic acid. The mechanism of adsorption would predict a behavior similar to the one observed.

#### Adsorption Equilibrium

It is observed in Figures 9, 10, and 11 that, regardless of temperature, equilibrium was obtained within 20 to 25 hours. In the actual recharge system, the concentration of silica at a given location is never able to attain equilibrium. As the silica is desorbed from the sediment matrix into the interstitial pore solution, it is carried

away by the infiltrating water. The system approaches a steady state condition of continual desorption and removal from the site.

According to the adsorption model, there are a finite number of adsorption sites, therefore, a finite amount of adsorbed silica. The concentration should then be continually decreasing with time as the adsorbed silica is attaining equilibrium. The maximum concentration of silica in the recharge water is observed within one day (Fig. 6), then the concentration decreases slowly for about 45 days. After about 45 days, the measured silica concentration is equivalent to that of the input water at the 0.5 m sampling depth.

#### Desorption Experiment

The following experiment was conducted to determine if the soil samples from the recharge area would conform to this adsorption model. The silica should be desorbable from the soil matrix in a sodium chloride solution until equilibrium is attained. Then if the solution is extracted and replaced with an identical silica from solution, equilibrium should be regained but at a lower concentration. A sodium chloride solution was used in order to promote clay flocculation and make water sediment separation possible without the use of a high-speed centrifuge.

The experiment was performed with three 10 gram samples of soil placed in 50 ml of 0.1 N NaCl and equilibrated at three temperatures: 1°C, 22°C, and 50°C. After allowing at least 48 hours for equilibration in all cases before extraction, the samples were centrifuged, and resuspended in a silica-free solution. Extractions were continued until a steady state was reached. The concentration is plotted for each extraction in Figure 13. The equilibrium concentration declines until the value is low enough to be attributed only to silica dissolution. This can be interpreted as the progressive removal of adsorbed silica. Adsorption equilibrium is dynamic, so that only a small per cent of the total amount of adsorbed silica is in solution at a given time. When this solution with its dissolved silica is removed, the equilibrium concentration must be reestablished from a smaller amount of material at the adsorbed silica sites. The increment of concentration decrease should be smaller as more solution containing silica is subsequently removed. This is observed in this experiment except for the first solution extract.

Since enough time had been allowed for equilibration, the low initial value would indicate that for some reason

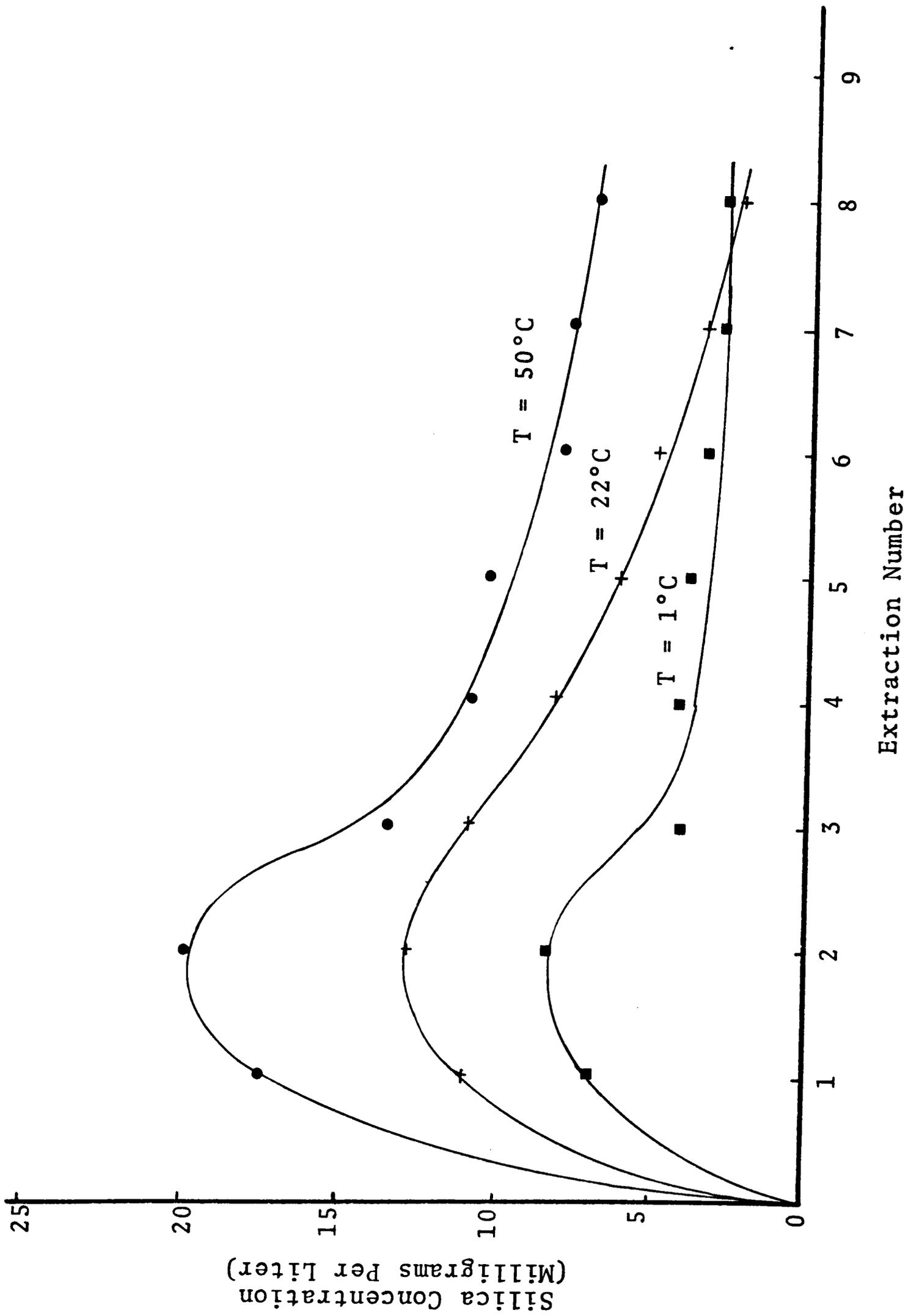


Fig. 13.--Silica concentration versus extractions.

silica was being removed from solution simultaneously with desorption by some method other than readsorption, such as anion fixation. It has been reported and summarized by Miller (1967) that the anions of phosphate, silica and nitrate are removed from soil solutions and fixed in the soil in a non-extractable form at neutral pH for many years. It was noted that soil sesquioxides of iron and aluminum as well as clays could be responsible for this anion fixation (Flach, Nettleton, Gile, Cady, 1969).

The chemical data from each sampling depth (Fig. 6) seems to indicate that silica is rapidly entering solution throughout the stratigraphic section. As the monomeric silica is removed from its locality of desorption, it remains in solution chemically unreactive, diminished only by dispersion, readsorption, or removal by clays and sesquioxides. If the recharge water were allowed to continue to infiltrate, the desorbed silica should be entirely removed from the soil system so that the remaining concentration of silica represents that of the input water, and decomposition and dissolution of clays and quartz.

## CHAPTER III

### ANIONIC BEHAVIOR OF SILICA AND FLUORIDE

#### Theory

The concentration of fluoride in potable water is important for use in a domestic water supply. Concentrations greater than 1 mg/l can cause mottling of the teeth (Dean, Dixon, and Coken, 1935) while values of about 1 mg/l are useful in preventing dental cavities (Dean, Arnold, and Elvove, 1942). The Southern High Plains of Texas and New Mexico have traditionally yielded ground water that exceeds the recommended concentration limit for fluoride (Cronin, 1964). It is of interest in the study of artificial recharge to be able to predict the concentration of fluoride in water that ultimately is available for consumption.

Water samples collected at several depths below the Lubbock Airport Recharge Basin indicate significant changes in concentration of fluoride with time, including both an increase and a decrease from the input value (Fig. 14). The question arises as to the nature of the sources and sinks of the fluoride in this system and what prediction about concentration variation can be made for future recharge locations.

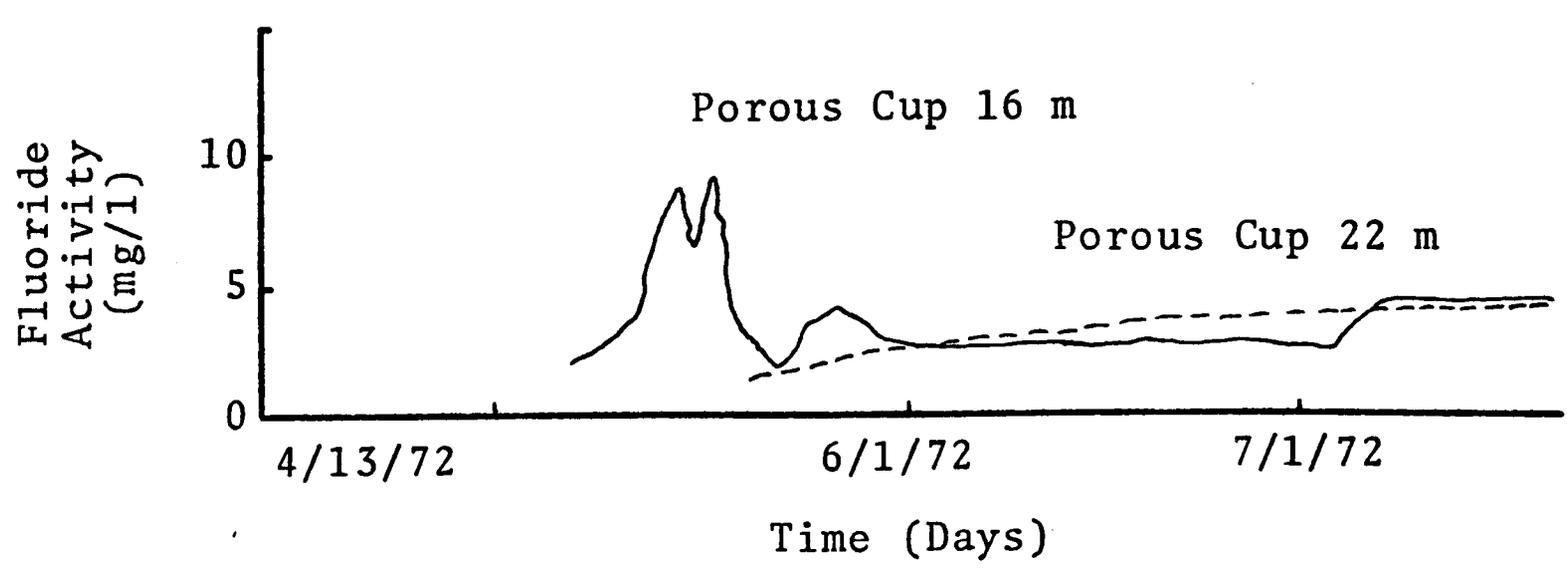
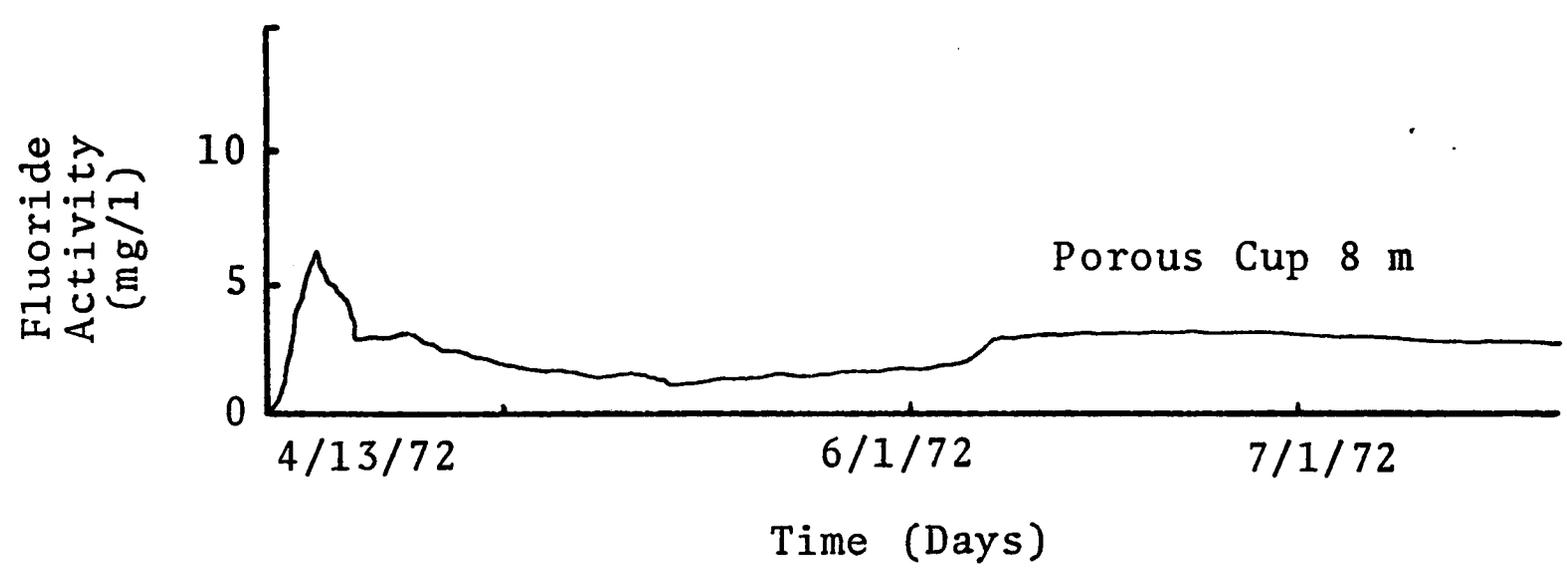
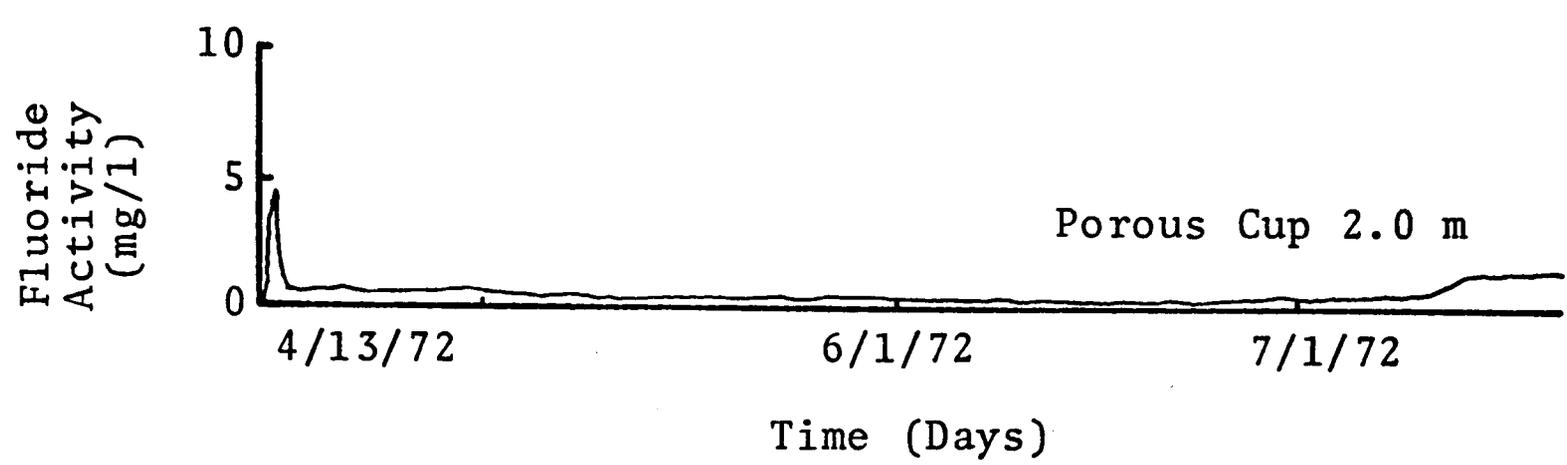
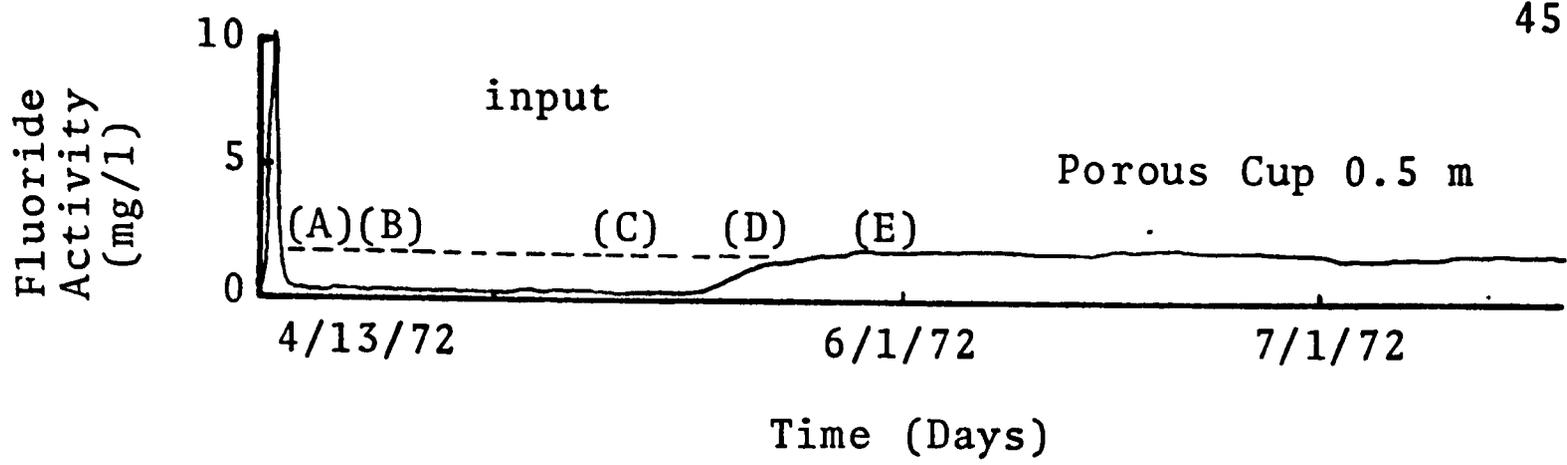


Fig. 14.--Fluoride activity in the first five porous cups.

The source for the initial rapid appearance of fluoride at the first sampling point (0.5 m) cannot be positively identified. X-ray diffraction data from material throughout the upper 8 m of the section failed to reveal any fluoride mineral. Heavy mineral separation, and petrographic studies also were unsuccessful. Several laboratory tests using different solutions failed to provide a solubility control that would indicate the source. It can be speculated that the fluoride is in the soil as a poorly crystalline, rapidly soluble fluoride salt of potassium or sodium. It is quite possible fluoride minerals of calcium and magnesium could be present in small quantities and yet be undetectable with the techniques and equipment available for this investigation.

### Anion Depletion

Several hypothesis appear to offer an explanation for the observed concentration depletion at the recharge site. Basically, there are five postulated mechanisms that control the concentration of anions in soil interstitial water.

1. Stoichiometric exchange of anions in solution for  $\text{OH}^-$  groups or other anions on the surfaces of clay minerals. The replacement of  $\text{OH}^-$  groups or other anions in iron and aluminum sesquioxides.

2. Attachment of polybasic acids such as phosphate and monosilicic acid to clay mineral surfaces.
3. Adsorption of anions into positions occupied by hydrated water molecules on clay edges, carbonates, and sesquioxides.
4. Solubility of various minerals.
5. Penetration of anions into the clay mineral lattice to replace  $\text{OH}^-$ ; or substitution of phosphate and silicic acid groups for silica tetrahedra.

No attempt will be made to relate the fifth mechanism to the recharged water. Evidence for lattice penetration is poor and generally unaccepted (Kurtz, DeTurk, and Bray, 1946); Romo and Roy, 1956).

Early work in anion exchange was related to phosphate in soils and its mechanism of fixation because of its agricultural importance. The common constituents involved in anion exchange reactions are  $\text{H}_4\text{SiO}_4$ ,  $\text{SO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ , and  $\text{F}^-$  (Grim, 1968; Kelley, 1943). This portion of the investigation has a two-fold purpose, to determine if any of the silica observed in the recharged water is a result of anion exchange, and secondly, to determine if anion exchange will explain the depletion of fluoride from the recharge water.

### Anion Exchange

The stoichiometric exchange of anions for attached

hydroxyl groups has been investigated for over 25 years. Black (1942), Dickman, and Bray (1941) have shown that fluoride replaced hydroxyls on kaolinite with a titratable increase in hydroxide concentration. It was hypothesized by several workers that fluoraluminate and fluorferrate minerals must be forming because the fluoride was not extractable and anions which are purely exchanged should be extractable (Kleiner, 1950; Sidgwick, 1950; Cotton and Wilkinson, 1962; Huang and Jackson, 1965).

Bower and Hatcher (1967) also reported that fluoride was adsorbed by various minerals in soil solutions, with a corresponding release of measurable hydroxide. The amount of fluoride exchanged was a function of the fluoride concentration in solution, and followed the Langmuir isotherm. The relative amounts of fluoride removed from minerals in soil are listed in Table 4, as experimentally determined by Bower and Hatcher (1967).

TABLE 4  
FLUORIDE ADSORPTION CAPACITY

<u>Soil Mineral</u>	<u>Fluoride Absorbed (mg) per Kilogram of Soil</u>
alkaline soils	59 - 120
gibbsite and kaolinite	190 - 295
halloysite	1400 - 1777
Al(OH) <sub>3</sub>	32,600
goethite, montmorillonite, vermiculite	only traces

The mechanism for the stoichiometric release of hydroxyl with corresponding replacement of phosphate is given in Figure 15. The attachment of silica and fluoride appear to be by the same mechanism (Kelly and Midgley, 1943).

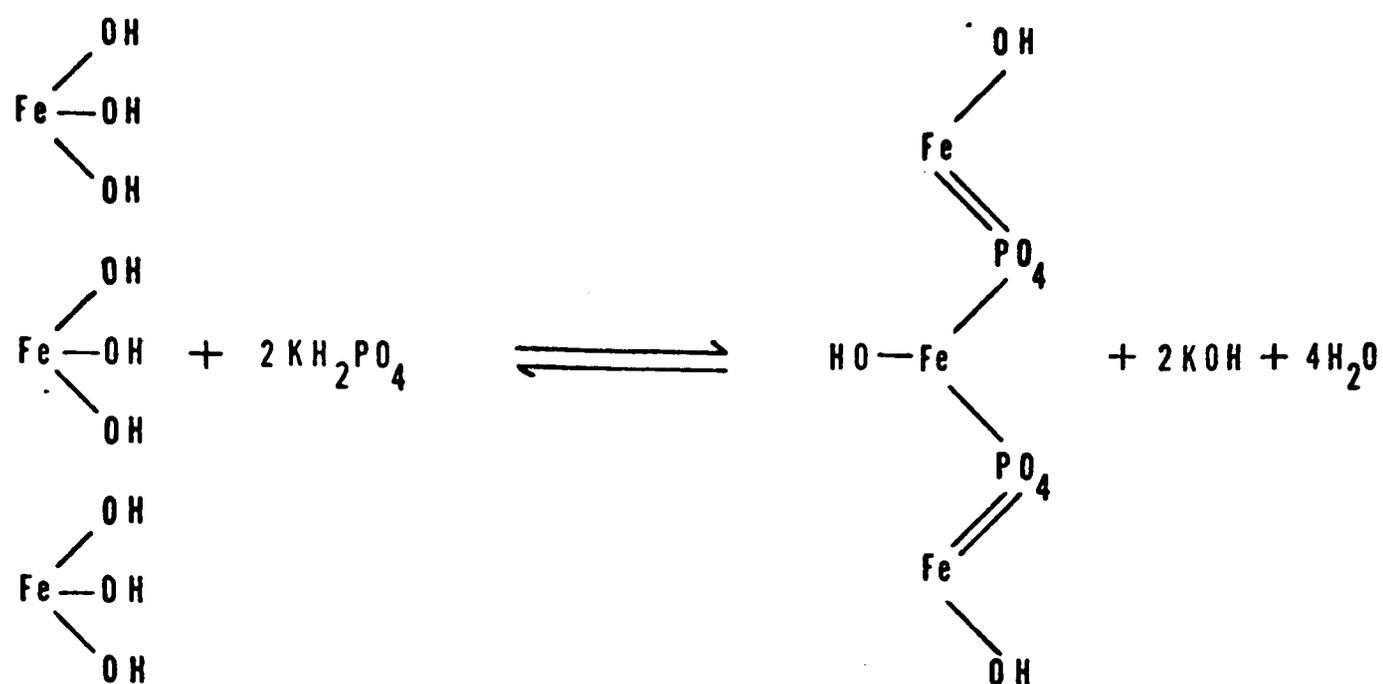
These models are for the exchange of  $\text{OH}^-$  by a variety of different anions. Helevy (1964) used isotopic oxygen in hydroxide and showed that true anion exchange does exist between hydroxyl groups on clay surfaces. The quantity observed was only 2 meq/100 gms, which is a quantity too small to explain the generally observed anion exchange in soils. This true exchange proposed by Helevy probably takes place with hydroxyl groups on the edge which are structurally different or have weaker bonds.

### Anion Attachment

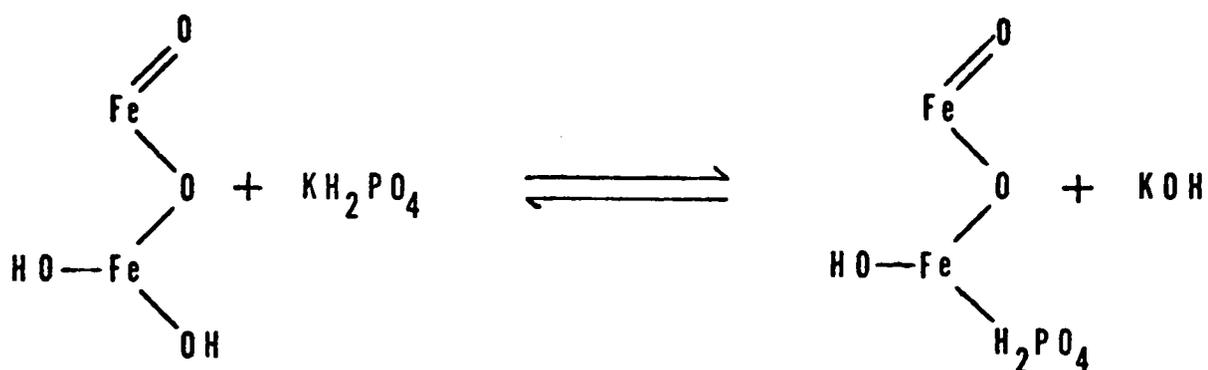
The second hypothesis postulates that anions may be adsorbed on soil mineral surfaces such as kaolinite or goethite, by means of potential determining ions such as  $\text{H}^+$  and  $\text{OH}^-$ . A net positive charge on the surface causes adsorption of anions and a net negative charge causes adsorption of cations (Hingston, Atkinson, Posner, and Quirk, 1968).

Accordingly, phosphate can exist in the soil in an exchangeable and non-exchangeable state (Fig. 16). The

## Ferric Hydroxide



## Limonite



## Kaolinite

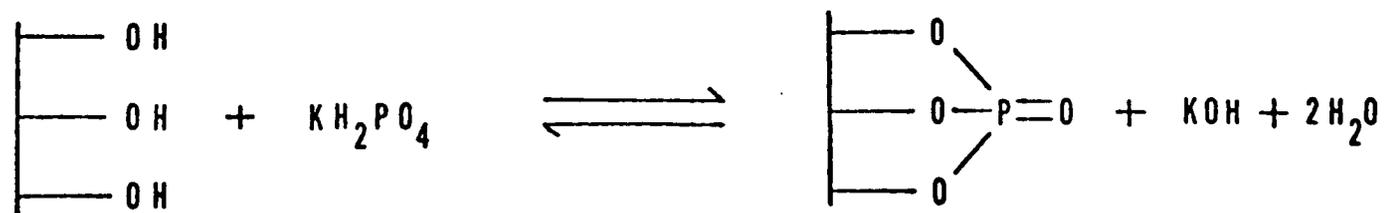


Fig. 15.--Replacement of hydroxyl by phosphate.

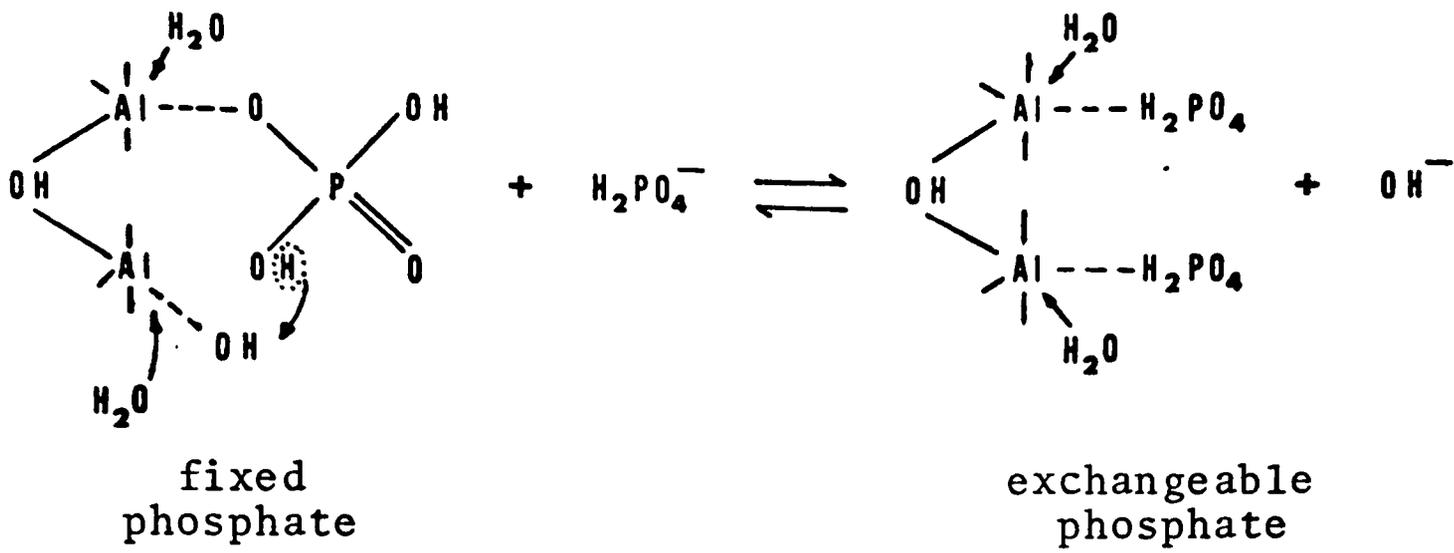


Fig. 16.--Ion attachment on clay mineral base.

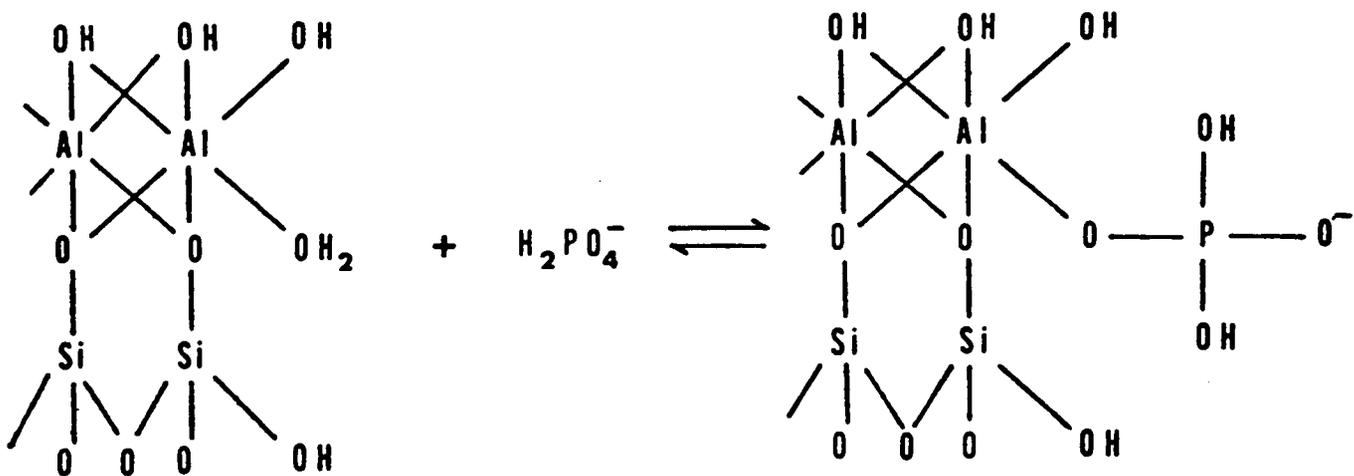


Fig. 17.--Replacement of attached water on clay mineral edges.

proposed attachment mechanism for phosphate is shown on the edge faces of a kaolinite mineral (Fig. 15) (Kafkafi, Posner, and Quirk, 1967).

### Replacement of Attached Water

The third type of anion depletion from soil solutions is by replacement of attached water molecules. Kuo and Lotse (1972) do not favor  $\text{OH}^-$  replacement of clays by coordinated anions such as phosphate and monosilicic acid, since the pH does not change significantly. They discount the other four proposed mechanisms and propose the following anion exchange mechanism with adsorbed water molecules. This exchange follows the Langmuir adsorption and is diagrammatically illustrated in Figure 17. Fluoride would presumably exchange by this same mechanism.

### Solubility Considerations

The summation of all the electrostatic interactions between ions is defined as the ionic strength (Moore, 1972). By knowing the ionic strength, the activity or actual effective concentration may be obtained. It is this concentration value which is involved in chemical reactions. Activity is determined by multiplying an activity coefficient ( $\gamma$ ) times the measured concentration. The following relations are used for ionic strength and activity calculation.

$$I = \frac{\sum m_i z_i^2}{2}$$

where

- m = Concentration of a given ion in moles per liter
- z = Charge of that ion
- I = Ionic strength

The Debye-Hückel equation may be used to calculate the activity coefficient for each ionic species. The activity coefficient when multiplied times the concentration yields the effective concentration or activity of the ion so that:

$$a = \gamma c$$

where

- a = Activity
- $\gamma$  = Activity coefficient
- c = Concentration.

The Debye-Hückel equation is expressed as:

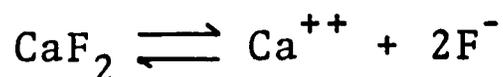
$$-\log \gamma_i = \frac{A x_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}}$$

where

- $\gamma_i$  = Activity coefficient of the ion  
 $A$  = Constant (for water)  
 $z_i$  = Ionic charge  
 $B$  = Constant (for water)  
 $a_i$  = Effective diameter  
 $I$  = Ionic strength.

Additional corrections to the ionic strength are made by considering the ions that are combined to form ion pairs and complex ions such as  $(\text{CaCO}_3)^0$ ,  $(\text{NaSO}_4)^0$ ,  $(\text{CaHCO}_3)^+$ ,  $(\text{CaOH})^+$ ,  $(\text{MgCO}_3)^0$ ,  $(\text{MgSO}_4)^0$ ,  $(\text{MgHCO}_3)^+$ , and  $(\text{MgOH})^+$ . Using dissociation constants given in Garrels and Christ (1965) it is possible to calculate the effect of ion pairing and complex ions on the activity of the solution.

When the ionic activity product ( $K_{iap}$ ) is calculated with activity values and compared to the solubility product constant ( $K_{sp}$ ), then the degree of supersaturation or undersaturation may be estimated. When the product of calcium activity and the square of the fluoride activity exceeds the  $K_{sp}$ , the solution is supersaturated and should precipitate calcium fluoride. For example, at saturation



$$K_{sp} = \frac{[\text{Ca}^{++}][\text{F}^-]^2}{\text{CaF}_2(\text{solid})} = [\text{Ca}^{++}][\text{F}^-]^2.$$

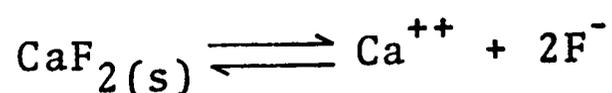
Therefore, when the ion activity product,  $[Ca^{++}][F^-]$  is greater than the  $K_{sp}$  the reaction reverses and  $CaF_2$  precipitates. If  $\frac{K_{iap}}{K_{sp}}$  is greater than 1, the solution is supersaturated, if less than 1, then the solution is undersaturated.

### Experimentation and Interpretation

Several preliminary experiments were conducted to obtain general information about the behavior of fluoride in the sediments from the recharge area. The results of the tests are summarized below.

### Solubility Control

Equilibrium calculations on the solubility of fluorite ( $CaF_2$ ) and sellaite ( $MgF_2$ ) in the recharge water were made to determine if precipitation of these minerals were responsible for lowering the observed fluoride concentration. A large amount of calcium and magnesium is introduced into the system from ion exchange and from other sources such as the solution of calcium sulphate from the soil formation. The larger concentration of calcium would push the equilibrium equation



to the left forcing precipitation of fluorite and lowering

the concentration of fluoride in the recharge water. Using the Debye-Hückel equation and then calculating the effect of ion pairing and ion complexing the following activity coefficients were obtained for the input water (Table 5).

TABLE 5  
ACTIVITY COEFFICIENTS FOR SALIENT IONS

<u>Ion</u>	<u>Activity <math>\gamma</math> Coefficient</u>
Mg <sup>++</sup>	0.62
Ca <sup>++</sup>	0.60
K <sup>+</sup>	0.87
Na <sup>+</sup>	0.87

It is not necessary to make a correction for fluoride activity because fluoride ions are measured with a specific-ion electrode which measures activity directly.

The solubility of NaF and KF, as well as the  $K_{sp}$  of MgF<sub>2</sub> and CaF<sub>2</sub>, are given in Table 6. The values are for equilibrium at 25°C in distilled water with zero ionic strength.

TABLE 6  
SOLUBILITY CONSTANTS FOR FLUORIDE SALTS

<u>Mineral</u>	<u>Solubility M/l</u>	<u><math>K_{sp} M^2/l</math></u>
Fluorite (CaF <sub>2</sub> )	$2.05 \times 10^{-2}$	$3.4 \times 10^{-11}$

TABLE 6 (Continued)

Sellaite ( $\text{MgF}_2$ )	$1.22 \times 10^{-1}$	$7.1 \times 10^{-9}$
KF	15.1	----
NaF	2.90	----

---

The calcium and fluoride ion activity is approximately 29 times saturation with respect to calcium fluoride in the first sample obtained from the 0.5 m sampling depth (Table 7). However, at no other time was saturation obtained with respect to either  $\text{CaF}_2$  or  $\text{MgF}_2$ . During the period of time from April 14 to May 17, the fluoride activity was between 0.1 and 0.2 mg/l (B and C, Fig. 14). The calcium and fluoride activities were less than one per cent of the saturation concentration during this same time; therefore, the concentration could not have been controlled by solubility of common fluoride minerals after the first day.

#### Lithologic Relationship

Earth material was collected at the spreading site by wire line core and hand auger. Material obtained from a depth of 0.5, 2.5, and 3.5 meters was mechanically sieved into six particle size fractions as listed in Table 8.

TABLE 7

## SOLUBILITY CALCULATIONS FOR FLUORIDE

<u>Date</u>	$\underline{\text{Ca}^{++}}$	$\underline{\text{Activity Mg}^{++} \text{ M/l}}$	$\underline{\text{F}^-}$	$\underline{\text{CaF}_2 \frac{K_{iap}}{K_{sp}}}$	$\underline{\text{MgF}_2 \frac{K_{iap}}{K_{sp}}}$
input	$0.928 \times 10^{-3}$	$0.662 \times 10^{-3}$	$0.463 \times 10^{-4}$	$0.580 \times 10^{-1}$	$0.20 \times 10^{-3}$
4-13-72	$0.389 \times 10^{-2}$	$0.36 \times 10^{-3}$	$0.505 \times 10^{-3}$	(A)29.2	$0.120 \times 10^{-1}$
4-14-72	$0.284 \times 10^{-2}$	$0.21 \times 10^{-3}$	$0.526 \times 10^{-5}$	(B)0.230 $\times 10^{-2}$	$0.818 \times 10^{-6}$
5-13-72	$0.135 \times 10^{-2}$	$0.66 \times 10^{-4}$	$0.526 \times 10^{-5}$	(C)0.110 $\times 10^{-2}$	$0.258 \times 10^{-6}$
5-20-72	$0.141 \times 10^{-2}$	$0.164 \times 10^{-3}$	$0.368 \times 10^{-4}$	(D)0.560 $\times 10^{-1}$	$0.313 \times 10^{-4}$
5-28-72	$0.108 \times 10^{-2}$	$0.638 \times 10^{-3}$	$0.47 \times 10^{-4}$	(E)0.701	$0.212 \times 10^{-2}$

TABLE 8  
FLUORIDE RESPONSE TO SIZE FRACTIONS

<u>Classification System</u>	<u>Diameter</u>	<u>Fluoride Activity</u>
Clay and Silt	less than 63 $\mu$	2.60
Very Fine Sand	63 $\mu$ to 125 $\mu$	2.65
Fine Sand	125 $\mu$ to 250 $\mu$	1.21
Medium Sand	250 $\mu$ to 500 $\mu$	1.20
Coarse Sand	500 $\mu$ to 1 mm	1.80
Very Coarse Sand	1 mm to 2 mm	1.72

Ten gram samples were removed from each fraction. After drying at 90°C, the samples were placed in 50 mls of distilled water and allowed to equilibrate. The final solution was tested for fluoride.

The results were similar for all three depths. The samples containing silt and very fine sand equilibrated at an average concentration of 2.6 mg/l fluoride. Fine and medium sand samples equilibrated at an average value of 1.2 mg/l, and coarse and very coarse samples at 1.8 mg/l. The coarse fraction yielded a higher concentration of fluoride because it contained a large percentage of clay aggregates which were broken up in solution. The samples composed of medium-sized particles contained principally

individual quartz grains.

### Fluoride Source Test

Samples obtained from a depth of 2.5 meters were 48% calcium carbonate, 15% clay, and the remainder quartz. Tests on three 15 gram samples of this material were conducted. One sample was diluted with 50 ml of distilled water, one with 50 ml of 2N ammonium hydroxide, and the third with 50 ml 2N acetic acid. The suspensions were stirred for thirty minutes, after which time an aliquot was withdrawn and mixed with an equal volume of total ionic strength buffer (Orion Research Inc., 1970) and tested for fluoride. The fluoride activity was monitored for several days to make certain that equilibrium had been attained. The fluoride activity equilibrated at 2.4 mg/l in distilled water, at 6.5 mg/l in the hydroxide solution, and 2.3 mg/l in the acetic acid solution. The conclusion from this experiment was that the fluoride is not related to the calcium carbonate by a simultaneous precipitation of calcium fluoride because the acidic solution and the distilled water gave similar values for fluoride activity. It was also concluded that the hydroxide was displacing the fluoride from the soil.

### Adsorption Experimentation and Interpretation

An experiment was conducted to determine if the

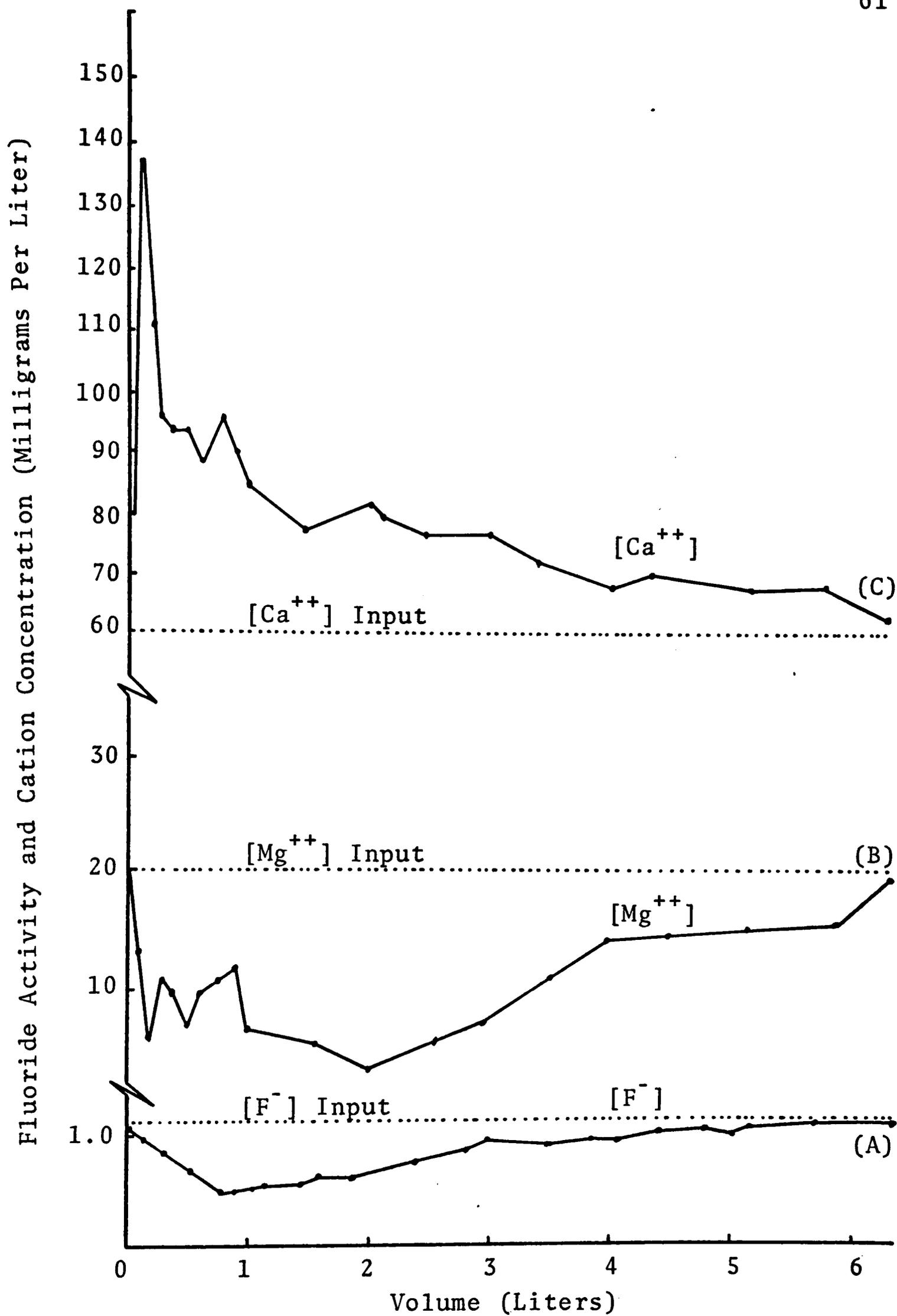


Fig. 18.--Column test.

fluoride activity changes observed at the artificial recharge site could be duplicated in the laboratory. Using the following technique the activity of fluoride could be monitored more frequently and the exact amount of soil and recharge water would be known. A small column was packed with 200 gms of soil material obtained from a depth of 0.5 meters, a point that corresponds to the depth of the first porous cup. Tap water, which is the same composition as the water used for recharge, was allowed to flow through the column. Repacking the column created a permeability which was much higher than that in the aquifer; consequently, water did not remain in the interstices as long as it would have in the natural section. The shape and intensity of the curve involving calcium and magnesium (Fig. 18) is smaller than that observed during recharge (Fig. 14) but the same general behavior is apparent. Fluoride dropped from an initial concentration of 1.1 mg/l in the tap water to a low value of 0.46 mg/l in the column effluent (Line A, Fig. 18). After 6.3 liters of water had passed through the column the soil no longer removed any fluoride from solution. The anion exchange capacity or adsorption capacity was satisfied at this point and the fluoride concentration of the effluent was equal to that of the input.

The calcium carbonate content was less than 1% in

the soil used for the column, and the pH of about 8.6 was stable; therefore, almost all of the calcium was contributed from the clay minerals through cation exchange.

This experiment provided a technique for determining the anion demand of a soil, analogous to the cation exchange capacity.

Since the absorption limit for fluoride can be attained, an experiment was conducted to determine if the exchange sites or adsorption sites could be satisfied by titrating a measured amount of soil material with a fluoride solution. A soil sample was obtained from a depth of 1.5 meters and oven-dried at 90°C, and ten grams were placed in a beaker with 50 mls of distilled water. The soil was continuously stirred with a magnetic stirrer and the activity of fluoride was monitored with a specific ion electrode. The suspension was titrated with a solution of 1000 mg/l  $F^-$  as NaF using a microburette. A concentrated titrant was chosen so that the volume change would be negligible. The values obtained are graphed with values obtained in a duplicate experiment performed on a solution of NaCl (Fig. 19). The specific conductance of the NaCl solution was the same as the soil solution; however, it did not contain soil in order to standardize the effect of ionic strength. The plot for the NaCl solution has been translated along the y axis to compensate for the

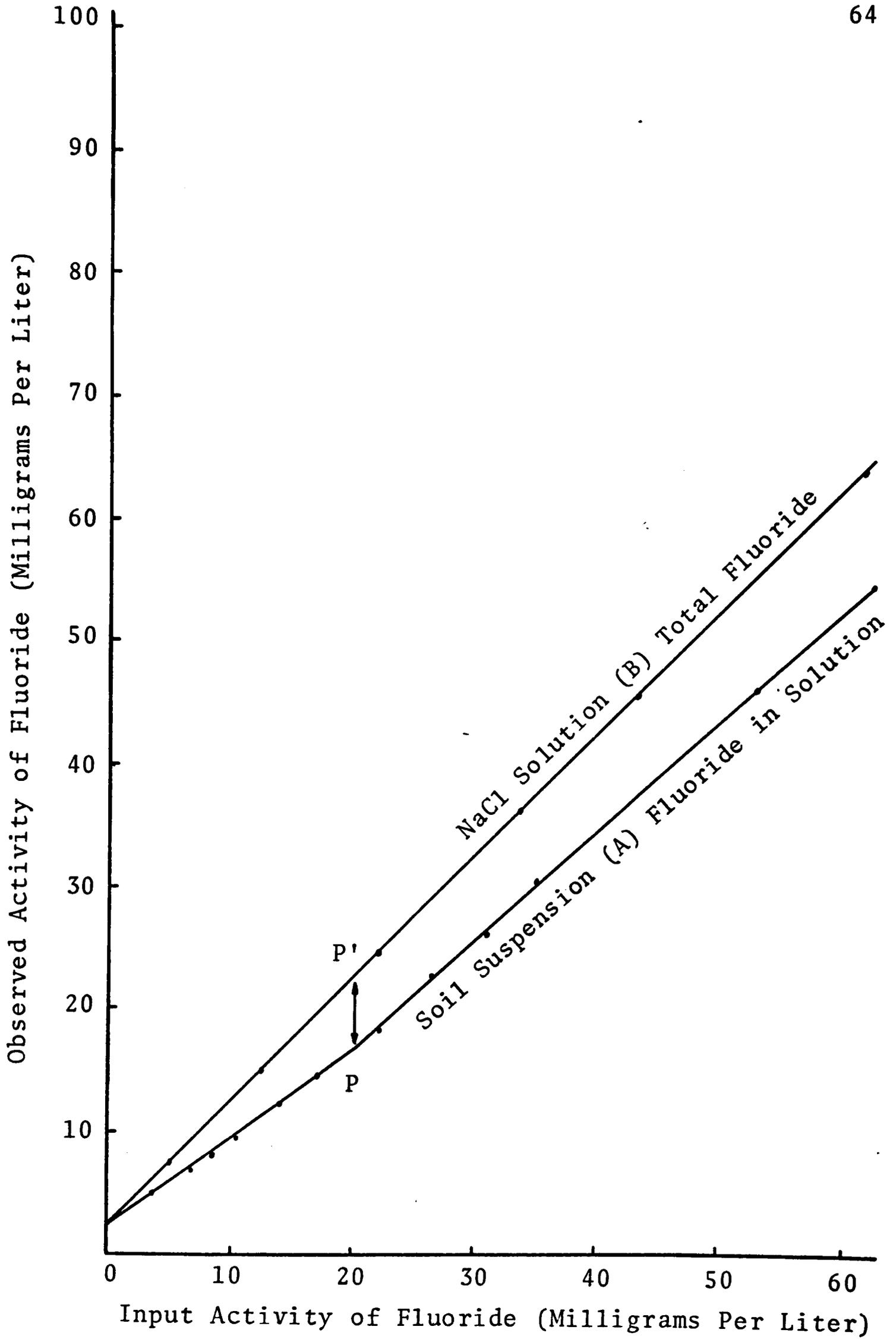


Fig. 19.--Anion capacity titration.

initial solution of fluoride from the soil slurry. Table 9 lists the fluoride activity observed in this experiment.

Input activity was plotted against observed activity so that if no reduction in the fluoride activity occurred the graph would yield a straight line with a slope of one. As shown in Figure 19, there is a break in slope of line A, indicating removal of fluoride by the soil.

TABLE 9  
ANION ADSORPTION EXPERIMENT

Standard NaCl mg/l	Soil-Slurry mg/l
0	0
2.45	----
3.55	4.75
----	5.20
6.80	6.70
8.60	8.00
10.50	9.50
14.00	12.00
17.00	14.70
22.00	18.25
26.50	22.50
31.00	26.00
35.00	30.50
53.00	46.00
70.00	61.00

The solution contained an initial fluoride activity of

1.9 mg/l. At point P there is an obvious change in the slope of line A (Fig. 19). Line B then represents the total amount of fluoride both in solution and adsorbed on the soil material. The difference between line B and line A is the amount, in mg/l, that was removed from solution. From line (P'-P) to the end of the titration the added fluoride departs from the theoretical line because of the solubility effects of other materials in the soil sample.

For this soil sample, an estimate is made for the fluoride concentration of 6.5 mg/l. This means that 32.5 micrograms of fluoride were removed per gram of soil or 325 milligrams per kilogram of soil. This roughly corresponds to an alkaline soil with a large percent of montmorillonite (Table 4) as determined by Bower and Hatcher (1967).

#### Adsorption Relationship and Mechanism

According to previously discussed mechanisms, both fluoride and monomeric silica can be attached to clay and soil mineral surfaces. The following experiment was conducted to see if the mechanism of attachment could be attributed to adsorption and if there was a relationship between fluoride and silica concentrations in the system. Five gram samples of soil taken from a depth of 2.5 meters were used for the experiment. This corresponds to a point just below the 2 meter sampling depth where the removal

of fluoride is observed to occur. Solutions containing a range of fluoride concentrations of 0-25 mg/l  $F^-$  as NaF and solutions of 0-60 mg/l  $SiO_2$  as  $Na_2SiO_3 \cdot SH_2O$  were prepared. The soil samples were added to the solutions and the concentration of silica and fluoride was measured after one hour which should allow time for anion exchange to occur. The input concentration in mg/l  $F^-$  and mg/l  $SiO_2$  is plotted against observed concentrations of fluoride and silica respectively. Deviation from a straight line indicates removal of the ions from solution (Fig. 20 and 21).

All of the standard solutions were adjusted to the proper concentrations in a 0.1N NaCl solution to compensate for ionic strength variations. Sodium chloride is reported to have some catalytic effect on silicate dissolution (Stöber, 1969); however, in one hour any such dissolution would be negligible. Line B, in Figures 20 and 21 is shifted upward along the y axis to compensate for silica and fluoride contributions from the soil.

The concentration difference between curve B and curve A (Fig. 20 and 21) represents the amount of silica or fluoride removed from solution. The number of milligrams ( $n_{ads}$ ) of either silica or fluoride adsorbed from solution at various concentrations can then be calculated. Using the Langmuir equation:

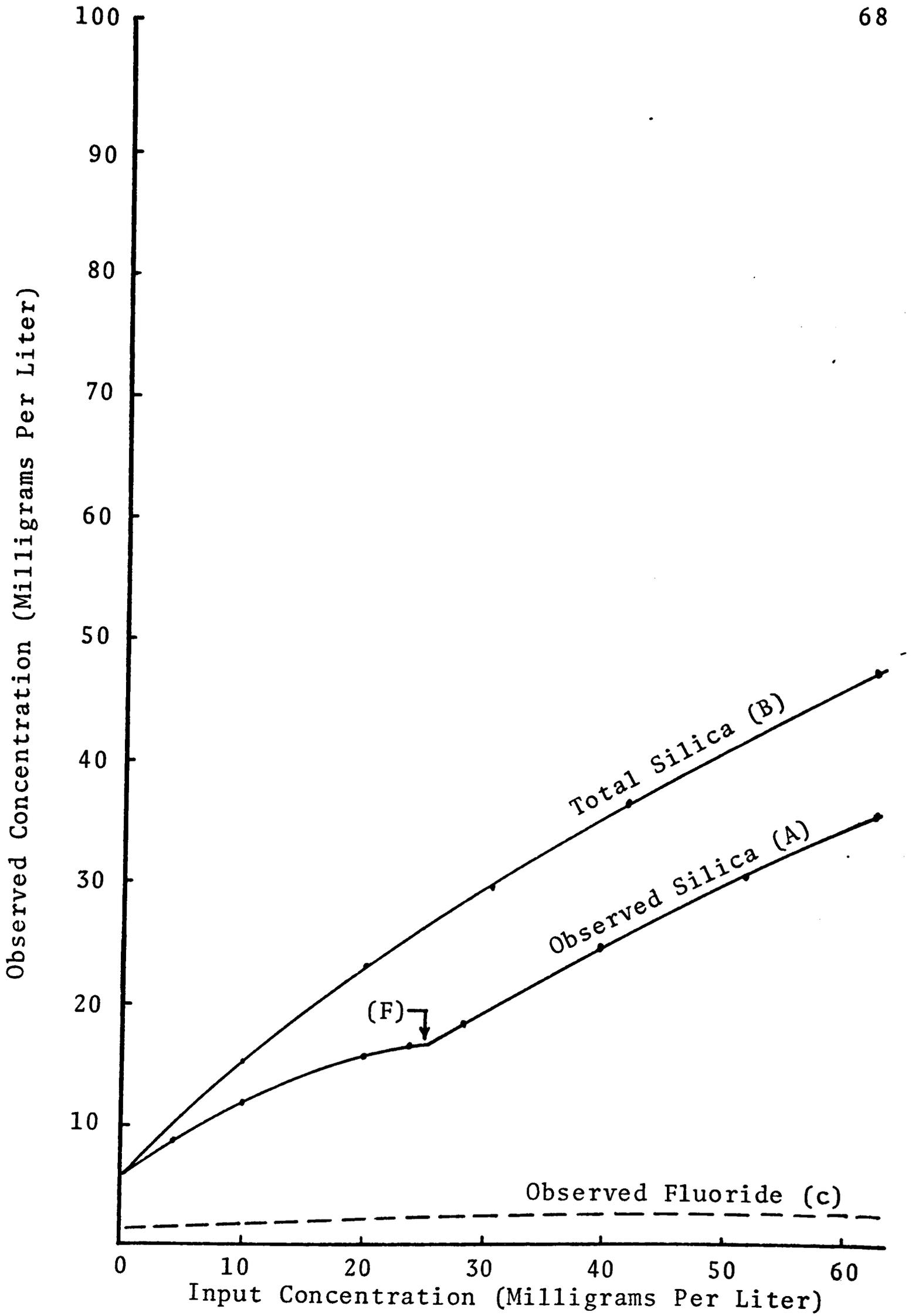


Fig. 20.--Adsorption control of silica concentration.

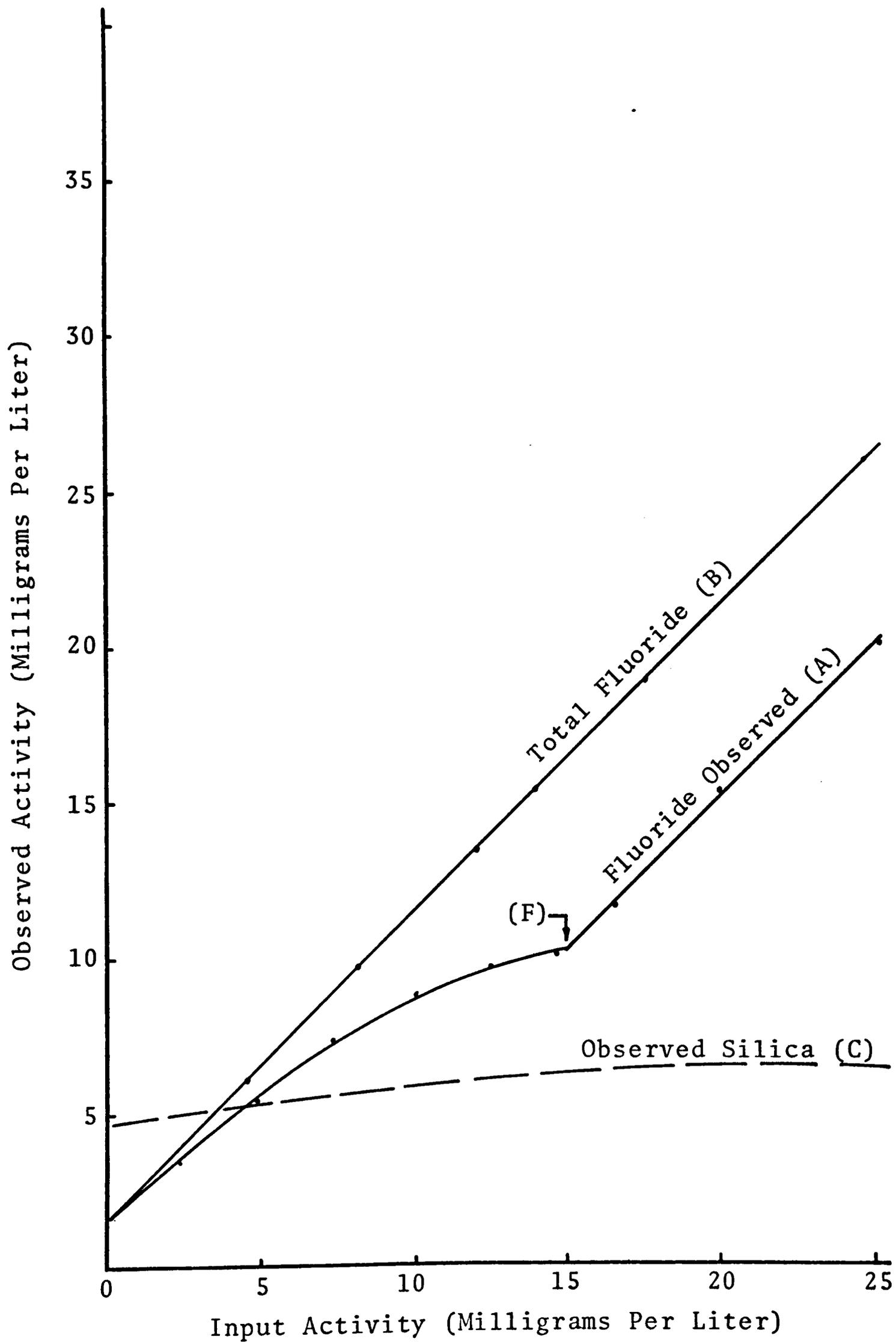


Fig. 21.--Adsorption control of fluoride activity.

$$\frac{n_{\text{ads}}}{n_o} = \frac{bc}{1 + bc}$$

also written

$$\frac{n_o}{n_{\text{ads}}} = \left( \begin{array}{c} 1 \\ - \\ b \end{array} \right) \left( \begin{array}{c} 1 \\ - \\ c \end{array} \right) + K_1$$

where

- $n_o$  = Maximum surface coverage
- $n_{\text{ads}}$  = Actual surface coverage
- $c$  = Equilibrium concentration
- $b$  = Langmuir constant
- $K_1$  = Proportionality constant,

then a test for adsorption can be made.

If  $n_o/n_{\text{ads}}$  is plotted against  $1/c$  (Fig. 22 and 23) then a straight line should be obtained with a slope of  $1/b$  if adsorption is the mechanism (Moore, 1972). In the case of both fluoride and silica, the attachment follows the Langmuir isotherm until the adsorption sites are filled (point F, Fig. 20 and 21), then the slope parallels the calibration curve because each silica addition remains in solution.

The silica concentration initially present in the soil

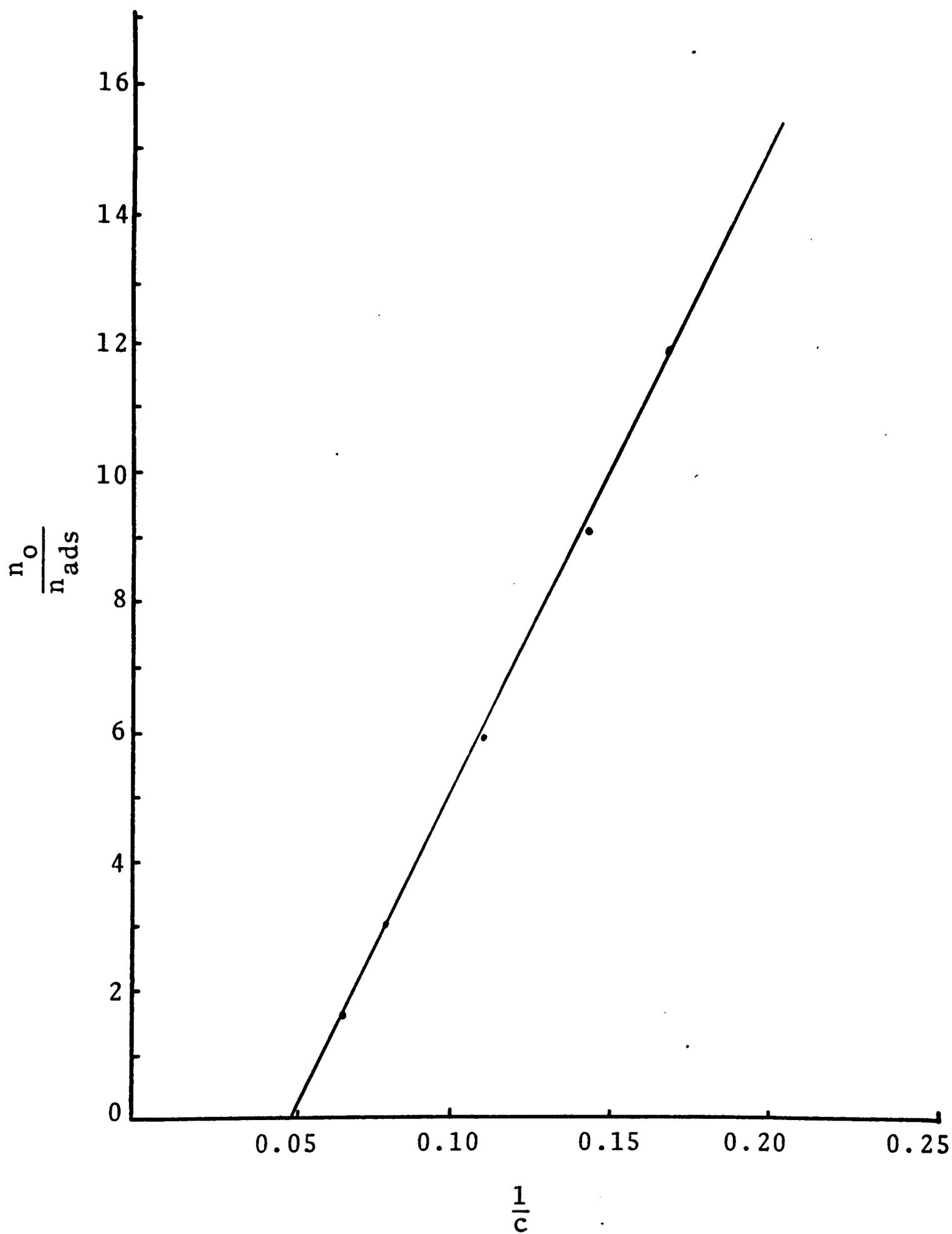


Fig. 22.--Langmuir isotherm for silica.

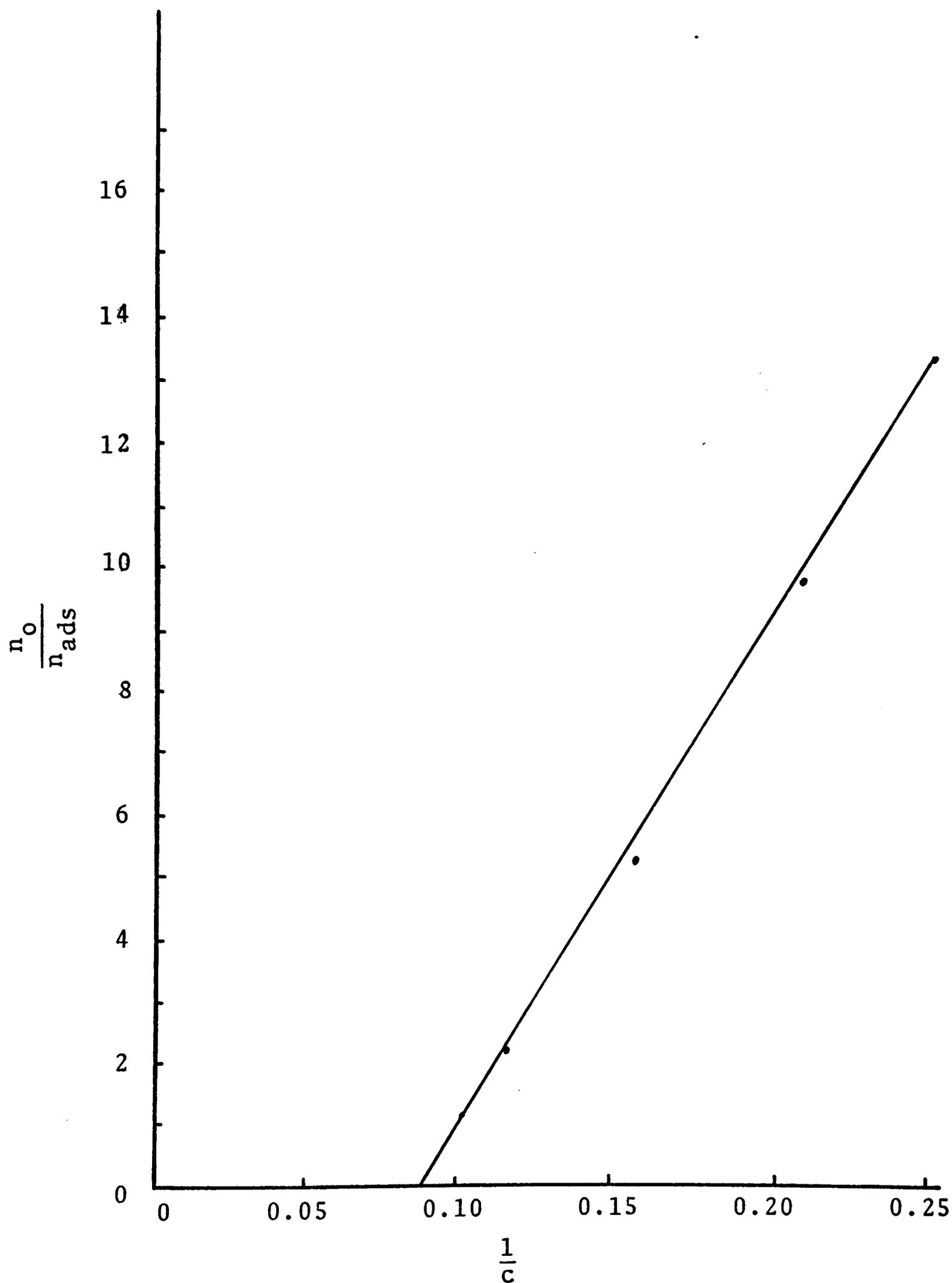


Fig. 23.--Langmuir isotherm for fluoride.

increased only a very slight amount with increasing fluoride activity; fluoride has the ability to displace silica when attached to clay surfaces or adsorbed on soil minerals in an exchangeable state (Fig. 21, curve 8). Because the increase in silica concentration is so slight, it may be assumed that the silica is not present in an exchangeable state on clay or soil mineral surfaces. The silica observed in the recharged water is derived almost completely from desorption of quartz grain surfaces.

The fluoride, if present in an exchangeable state, should be displaced by the higher silica concentrations (Fig. 20, C). Instead fluoride remains unchanged with increased silica concentrations.

The concentration of fluoride in the recharge water is controlled by adsorption onto clay surfaces and sesquioxide attachment sites. The source for fluoride is some rapidly soluble form not related to the clays or sesquioxides. There is a definite capacity for removal of fluoride; at a given concentration, an equilibrium amount will be removed according to the Langmuir isotherm until the capacity is satisfied.

## CHAPTER IV

### PREDICTABILITY

#### Silica Predictability

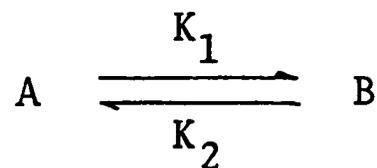
The attachment mechanism for monomeric silica on silicate surfaces such as quartz is proposed to be an adsorption phenomenon. Laboratory experiments indicate that silica is both adsorbed and desorbed in a manner described by the Langmuir isotherm. The effects of change in silica concentration with water volume were studied in both equilibrium experiments and in a column experiment under dynamic change. These tests showed that there is a finite amount of monosilicic acid adsorbed on the quartz surfaces which can be completely removed by infiltrating water. The movement of the desorbed silica through the geologic section is analogous to the process of chromatographic elution.

Chromatography is a process of component separation in heterogeneous equilibrium as a mobile phase passes through a stationary phase (Dvorak, Hais, Tockstein, 1963). In this investigation the mobile phase is monosilicic acid transported in water, the stationary phase is considered only as adsorbed silica on the quartz sand matrix.

When an undersaturated mobile phase reaches the spot where molecules are available for removal (point  $X_0$ , Fig.

26), desorption is initiated and previously attached molecules enter the mobile phase. If the rate of flow is slow enough a distribution equilibrium is established. The molecules which passed into the mobile phase are carried farther on. The concentration of substances in the stationary phase is no longer in equilibrium with the new mobile phase, so molecular transfer attempts to again establish equilibrium. In this manner the adsorbed substance originally present is gradually removed or eluted and re-adsorbed farther along in a stepwise process.

The successive adsorption and desorption represents a continuous transition between two phases which can be reduced to a simple kinetic expression



where A represents the adsorbed phase and B represents the mobile phase.

The mathematical explanation for the equilibrium situation is a Gaussian distribution, so that at point  $X_1$  (Fig. 24) the rate of  $A \leftrightarrow B$  equals the rate of  $B \rightarrow A$ .

If the soil matrix were silica free and an increment of recharge water containing a high silica concentration were injected, the amount of silica in the adsorbed phase

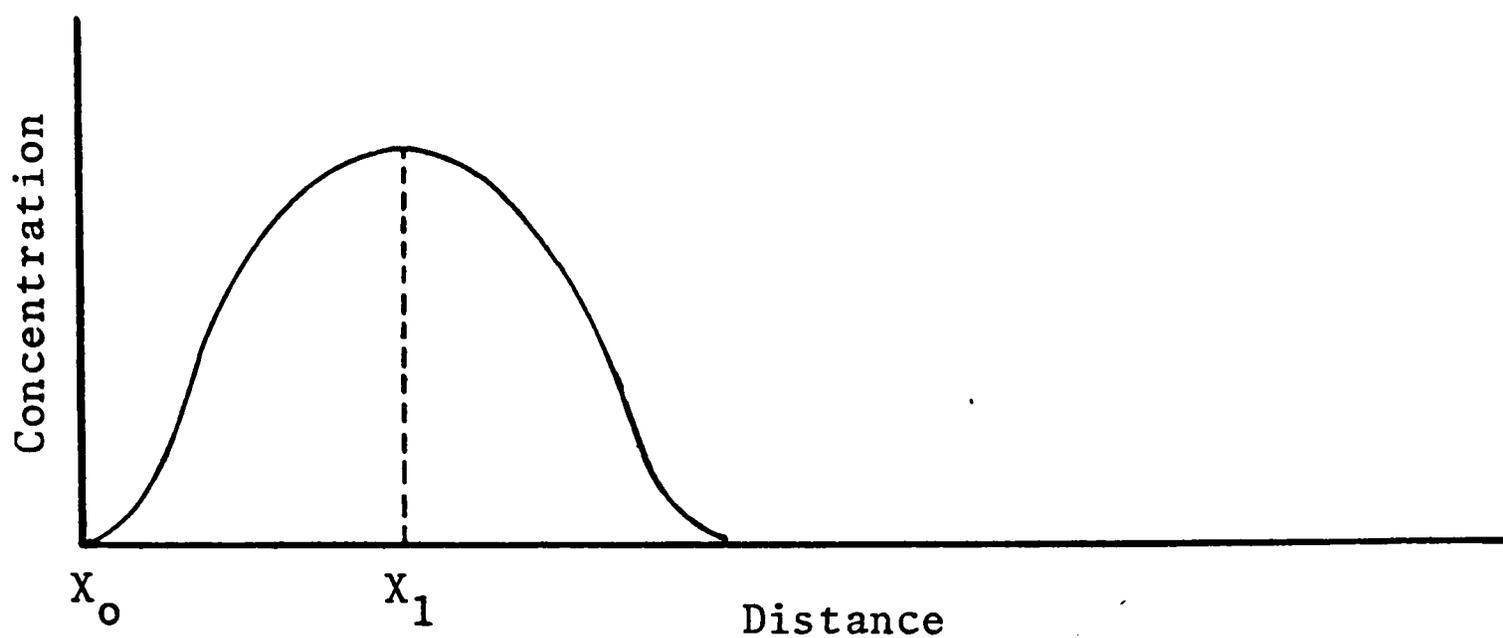


Fig. 24.--A Gaussian distribution for adsorbed material.

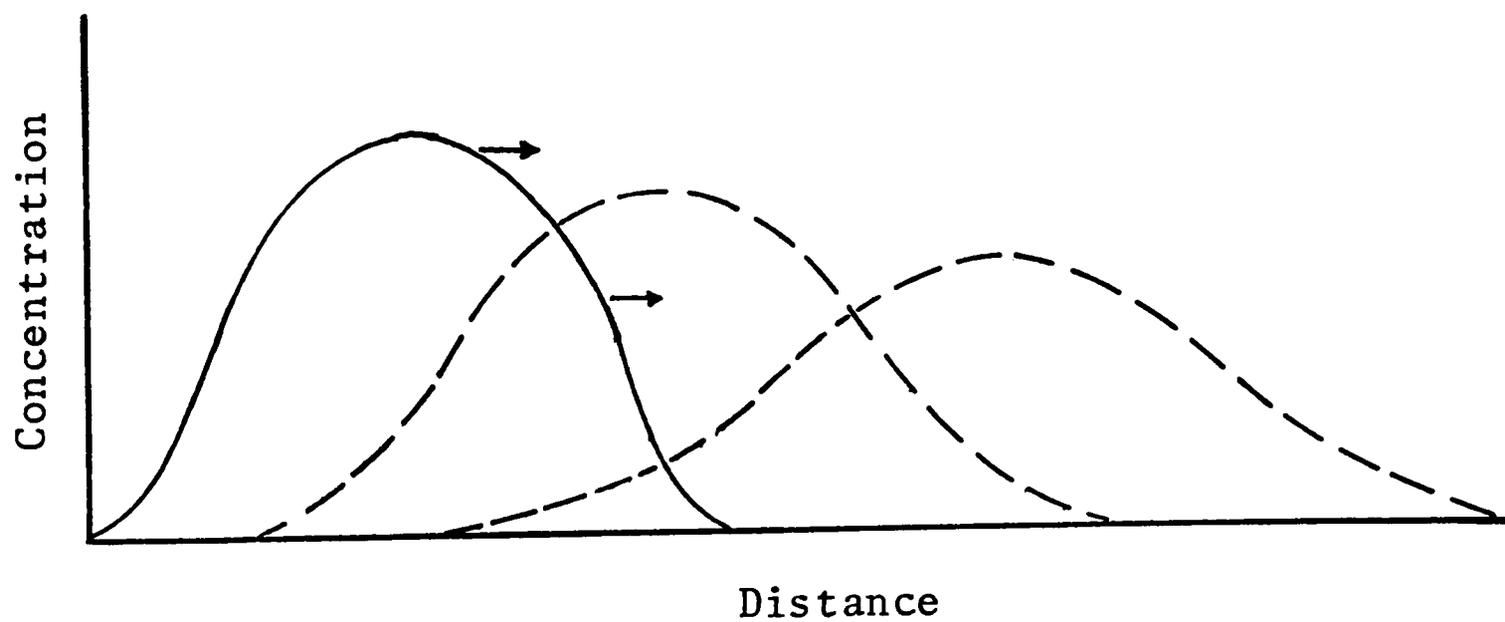


Fig. 25.--Adsorption equilibrium versus distance.

would increase until the adsorption sites were saturated. The increment of injected silica would move through the geologic system as a Gaussian distribution curve (Fig. 25) (Giddings, 1959). After some period of time diffusion would cause broadening of the peak.

Observations at the recharge site are of the opposite situation. The geologic column has adsorbed silica present and the input water is essentially silica free. As the water infiltrates, the adsorbed silica quickly seeks equilibrium and assumes a Gaussian shaped curve representing silica concentration in solution with respect to time. As the silica is removed from the adsorbed phase, it enters solution until equilibrium is attained, is transported and then re-adsorbs on impoverished adsorption sites farther down the column (Fig. 26). A succession of curves would be observed until the material is completely removed.

The trailing edge of the curve (Fig. 26) represents a concentration not yet at equilibrium, so it lags behind; the leading edge has surplus concentration and moves ahead more rapidly. The net result is spreading of the two edges away from the center; however, the area under the curve which represents the amount of material involved, remains constant (Giddings, 1959).

If the change in concentration with time is monitored

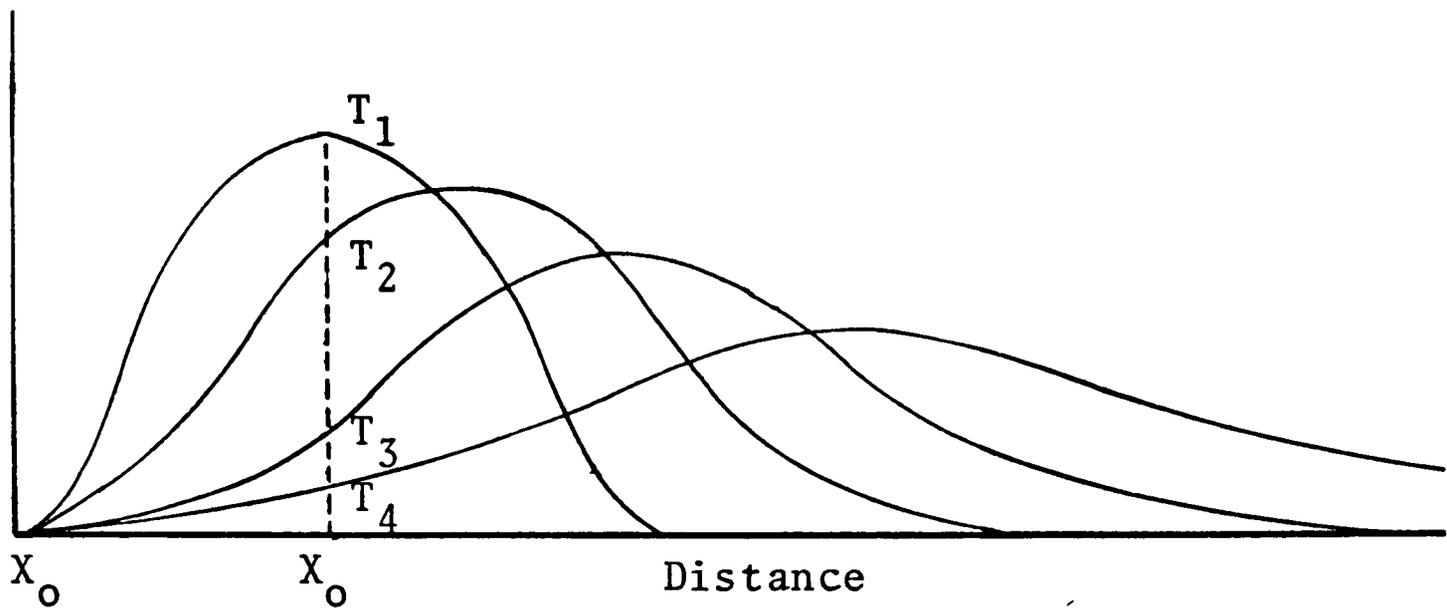


Fig. 26.--Desorption versus distance.

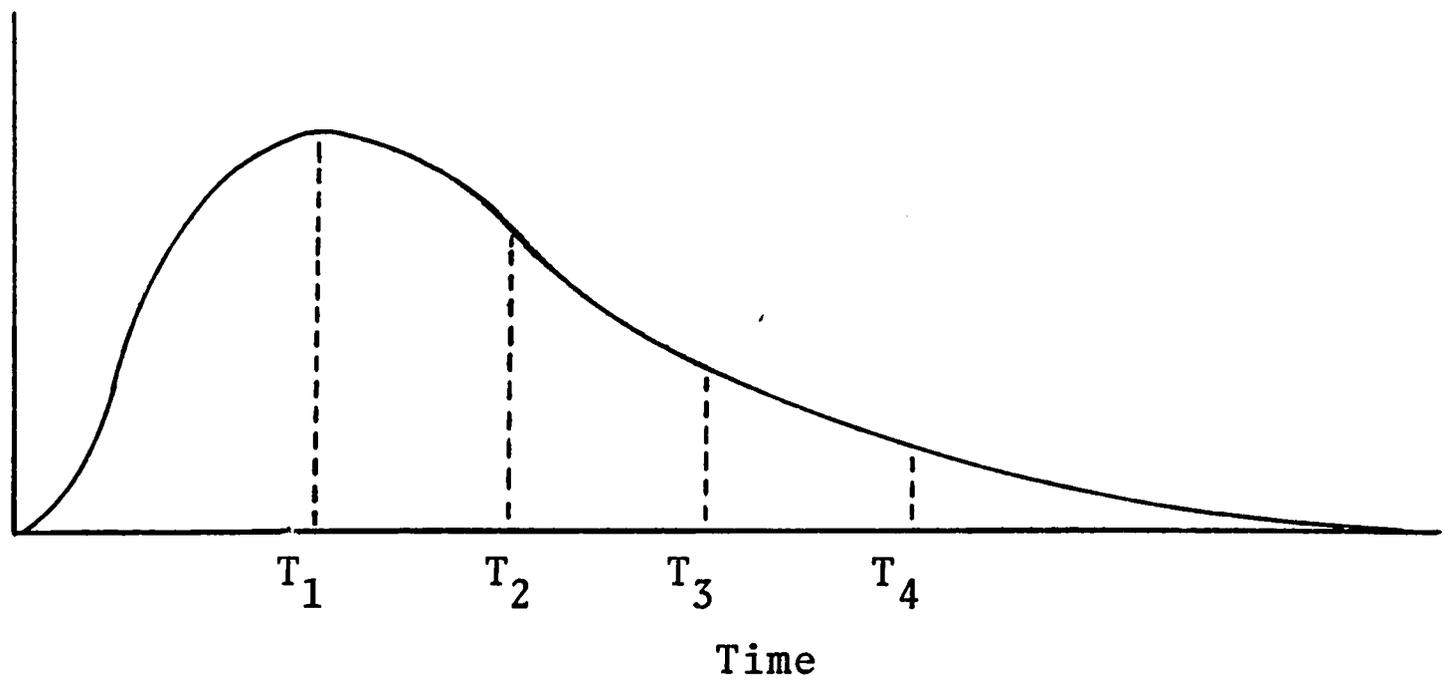


Fig. 27.--Changes in concentration versus time.

at some fixed distance along the curve (point  $X_1$ , Fig. 26), then a concentration versus time curve is observed (Fig. 27).

This curve illustrates that the system rapidly seeks equilibrium, then the material is removed at a decreasing rate according to the Langmuir isotherm. The more material removed, the lower the steady state concentration and the more slowly the desorbable material is removed. This type of curve represents observations at several sampling depths at the recharge site. Observations made from a fixed depth in the geologic section can be seen from Figure 6. The mechanism is well illustrated in the first and second sampling depths but by the time the "elution" has reached the third and fourth sampling depths (Fig. 6) the saturation value has been attained and a truncated curve is observed. This condition will continue until the silica is washed from the system. A similar curve was observed in the column study and is shown in Figure 28.

In a system such as the one studied in the investigation, it should be possible to gain enough information to predict how the concentration of monosilicic acid changes with infiltrated volume of water and with time at other sites of potential artificial recharge.

The actual numerical model is beyond the scope of this

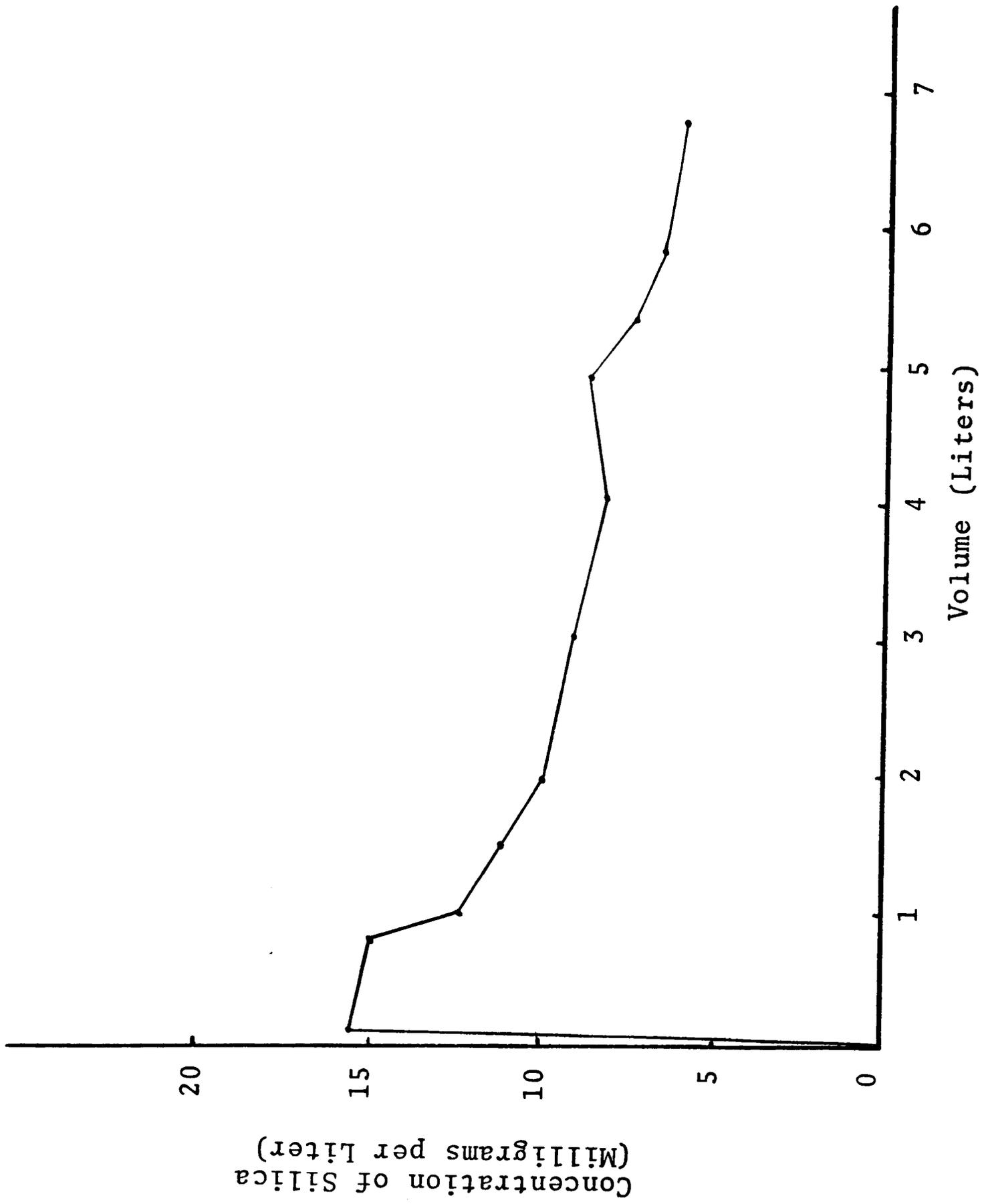


Fig. 28. --Observed change in concentration of silica with volume in the column study.

investigation, but a fundamental expression of balance, valid for any point in a chromatographic column has been derived for the quantity of substance passing from one phase to another and is given below (Wilson, 1940; De Vault, 1943).

$$\left( \frac{\partial c}{\partial x} \right)_v + \left[ A_m + A_s f^1(c) \right] \left( \frac{\partial c}{\partial v} \right)_x = 0$$

where

- c = Concentration
- x = Flow distance
- v = Volume
- $A_m$  = Cross-sectional area of the mobile phase
- $A_s$  = Cross-sectional area of the stationary phase.

This relation is the material balance equation which states that the sum of material loss from one phase and the material gain for another is constant. It is necessary to know the porosity of the formation, chemical properties of the material, specific surface area, infiltration rate, total volume, input concentration, total amount of adsorbed silica, and available adsorption sites to solve such an equation. Most of this information is obtainable or may be approximated. In general, the curve representing the change in concentration with time can be approximated by

Figure 27.

### Fluoride Predictability

The behavior of fluoride in the system investigated is the inverse of the silica behavior. The soil matrix has a great number of available exchange and adsorption sites for anions on clay minerals and hydrated soil sesquioxides surfaces. The initial concentration of fluoride, though low by water-quality standards, is still sufficiently high to force reaction with the adsorption sites in the soil.

The adsorption of fluoride from solution follows a curve similar to the Langmuir isotherm curve (Fig. 21 and 23). The fluoride is actually exchanged with adsorbed water, which is reversibly adsorbed, and is exchanged for hydroxide on sesquioxides and clay minerals which does not seem to be easily reversible under the same conditions. Nitrate, phosphate, and hydroxide will replace fluoride in this "unextractable" state when they are present in much higher concentrations. Both in the column study and in the actual recharge situation, fluoride is removed almost completely from the infiltration water until the "anion retention" capacity is satisfied (Fig. 14 and 18).

A theoretical model can be constructed to predict what the behavior of fluoride will be in a new area for

recharge. The total amount of fluoride that will be removed at a given input concentration per unit weight of soil can best be determined through a column study. If representative samples are used for the study, average values for adsorption capacity can be interpolated for the geologic section.

In a soil column study the fluoride is removed quickly and almost completely until the sorption sites are filled. If several columns of soil were saturated with input water containing various concentrations of fluoride, then a Langmuir isotherm can be drawn to represent the behavior of that soil (Fig. 23).

The recharge water removed about 90% of the fluoride per unit volume from the input water at the spreading site during the early phase of the test. If the water that infiltrated during recharge actually came in uniform activity and made continuous contact with all the sorption sites, then probably most of the fluoride would have been removed. If the adsorption capacity is known, then a prediction can be made as to the total volume of water that can be recharged before the adsorption capacity for fluoride is satisfied. Figure 29 is a graph of the observed number of kilograms of fluoride removed per day from the first 0.5 m of soil at the recharge site; the input water has an

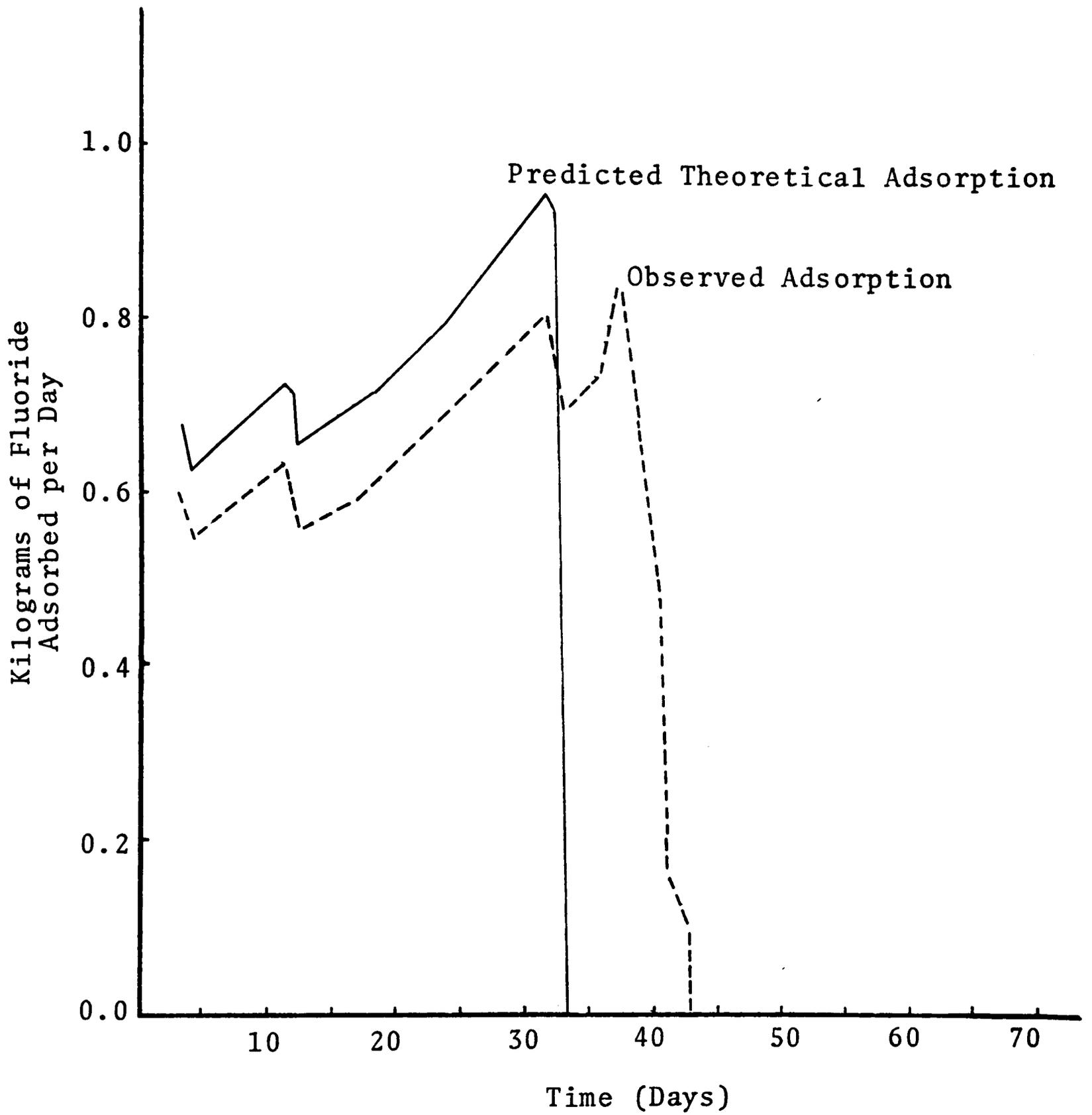


Fig. 29.--Observed and predicted fluoride activity.

average activity of 0.8 mg/l  $F^-$ . The theoretical amount of fluoride that should have been removed per day is given by line B (Fig. 29). Close agreement between observed and predicted value was obtained. From the time that the adsorption capacity was attained until the termination of recharge operations, the fluoride concentration observed at the 0.5 m sampling interval remained the same as the input concentration (Fig. 14).

In each of the other sampling intervals the same general decrease in fluoride concentration is observed, but the decrease tends to be less pronounced because of the higher overall concentration of fluoride (Fig. 13). Each porous cup collects samples that show the cumulative effect of the shallower positions. The readily soluble fluoride minerals present throughout the geologic column keep the fluoride concentration above input with increasing depth, but the effect of adsorption is demonstrated by the depressed early portion of the curve (Fig. 14). Eventually, the sorption sites will be filled, the rapidly soluble fluoride phase will be washed from the system, and the observed porous cup values will correspond to the input concentration.

## CHAPTER V

### SUMMARY AND CONCLUSIONS

The constituents of silica and fluoride as observed in the recharged water respond differently, but obey the same basic phenomenon of adsorption and desorption.

The monosilicic acid molecule which is initially adsorbed on the surface of quartz sand grains, is eluted through the geologic section by the recharge water. The solubility of silica polymorphs is too slow to contribute significantly to this phenomenon. The rapid desorption process yields an unusually high concentration of  $\text{SiO}_2$  in a very short time which is washed through the unsaturated zone to the water table. Monosilicic acid is adsorbed in a normally non-extractable form on clay minerals; consequently, clays and soil minerals, other than quartz, do not significantly contribute silica to the system. It should be possible to construct a mathematical model which would predict the changes in concentration of silica by using the mass balance equation and elution curve equations since all of the parameters are attainable.

The fluoride ion, even though present in low concentrations, is effectively removed from the recharge water by clay minerals and sesquioxides. Slightly soluble

fluoride salts do not control the observed concentration fluctuations of fluoride after the initial rapidly soluble fluoride salts are removed. The exchange of fluoride for hydroxyl groups and water molecules on clay mineral, hydrated iron, and aluminum sesquioxides surfaces follows the Langmuir isotherm curve. The capacity for anion removal of fluoride can be predicted. Predictions should apply to the initial stage of recharge operations as well as after long-term flow.

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