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ANION REPLACEMENT REACTIONS FOR THE REMOVAL OF STRONTIUM FROM AQUEOUS SOLUTIONS

L. L. AMES, Jr.

JULY 5, 1960

HANFORD LABORATORIES

HANFORD ATOMIC PRODUCTS OPERATION
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By

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Chemical Research and Development Operation
Geochemical and Geophysical Research

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TABLE OF CONTENTS

Page

ANION REPLACEMENT REACTIONS FOR THE REMOVAL OF STRONTIUM FROM AQUEOUS SOLUTIONS

ABSTRACT

The replacement reactions that could be adapted to the removal of strontium from aqueous solutions were investigated. The kinetic anion replacement systems calcite-phosphate, calcite-fluoride, gypsum-carbonate and gypsum-phosphate are discussed along with concomitant Sr^{+2} inclusion into the final product. In a system containing several anions, only a single, least-soluble compound containing the available cation is stable. The replacement reaction rate is directly proportional to the solubility difference between the original solid and final product. Several other variables also affect the reaction rate including temperature, influent pH, surface area of the initial solid, concentration of extraneous ions, and concentration of active anion. These variables affect diffusion rates to and from reaction sites as well as differences in solubility between initial and final reaction products. The crystal structure of the resulting product greatly affects the concomitant removal rate of Sr^{+2} into the resulting product.

INTRODUCTION

Minerals are seldom simple chemical compounds. Isomorphous substitution is the rule rather than the exception. Any cation may isomorphously substitute for any other if two conditions are fulfilled: 1) steric conditions allow the cation to substitute into a given structure, i.e., the cation "fits the available hole," 2) electrostatic neutrality results when the cation is accepted into the given structure.(9) This latter condition may be satisfied in several ways. For example, two three-valent cations may substitute for three two-valent cations as well as single and direct substitutions.

It is fundamentally confusing and wrong to consider a mineral a chemical molecule. Such a concept leads to the postulation of series "end-members" that, in the case of complex substitutions, become extremely unwieldy.

The apatites, applying the end-member concept, would require several series to explain the derivation of (Ca, Mg, Sr, Ba, Pb, Zn, trivalent rare earths, Na_2, $K_2)_{10}(PO_4, AsO_4, CO_3)_6(OH, F, Cl)_2$ from $Ca_{10}(PO_4)_6(OH)_2$. Considered structurally, the seemingly bewildering array of isomorphous substitutions becomes relatively simple to understand.

The mineral apatite is spatially arranged in a characteristic structure in which the spatial and charge requirements for a cation to occupy the site usually filled by Ca^{+2} are broader than for an analogous Ca^{+2} site in other structures. For this reason apatite allows a wide range of complex substitutions. An apatite "molecule," as such, does not exist. What does exist is an apatite "frame work" into whose Ca^{+2} position, or "hole" several other cations may fit in many ratios and proportions.

If our object is to remove Sr^{+2} from aqueous solutions, apatite could accomplish this object by two fundamentally different processes. The first of these processes is simple cation exchange; i.e., an existing Ca^{+2} on the external surface of an apatite grain can be displaced by a Sr^{+2} from the aqueous solution. The capacity of the apatite to adsorb Sr^{+2} is exhausted relatively rapidly, however, and the strontium remaining on the apatite is easily removed by reversing the exchange process. There is another process that will remove strontium from aqueous solutions as readily as cation exchange, and also "fix" the strontium as well. This process is called metasomatic replacement, or simply replacement. It is an extremely common process in nature and involves the alteration of one mineral structure to that of another with or without the addition and subtraction of ions into the existing structure. This process of structural rearrangement usually takes place at an interface between the initial and final structure. It is at this interface that strontium may be included in a Ca^{+2} position in the forming apatite, not by physically displacing a Ca^{+2} as in the cation exchange process, but by fitting into a structural position that also could have been filled by calcium. The Sr^{+2} so removed is, for the most part, "buried" in the interior of the forming apatite crystal, and hence is not subject to removal by a cation exchange process.

It is the purpose of this paper to investigate some of the general principles governing anion replacement reactions, and their relationship to concomitant strontium removal rate into the final replacement product. The results may help to evaluate the applicability of these reactions to the removal of radiostrontium from aqueous radioactive waste solutions with resulting reduction in stored volume.

SUMMARY

The solubility difference in a given system between the original solid and a possible alteration product determines whether or not a given replacement reaction will occur, and determines the rate at which the reaction will occur. Given several possible alteration products less soluble than the original solid, only the least soluble product is stable in the system. The data clearly show only one final product for each multiple anion system containing one cation. The rate at which this final product forms is directly proportional to the difference in solubility between the initial and final product. The removal of strontium always increases with increasing pH. However, the crystal structure of the final product exerts the greater effect on strontium removal. The best decontamination values for strontium were obtained when the crystal lattice types of the strontium and including calcium compounds were identical. The total effect of changes in the system variables on strontium removal rate was additive. The results show that it is possible to attain very large strontium decontamination factors by manipulation of the variables of these anion replacement reactions. The resulting reaction product fixes the strontium in the crystal lattice by isomorphous substitution of Sr^{+2} for Ca^{+2}, but may release this strontium if the reaction is reversed.

Several advantages over scavenging and possibly direct calcination techniques are apparent from the applications of the reactions to column use. These advantages include: 1) a potentially very large volume reduction, 2) removal of strontium from aqueous solutions containing large concentrations of extraneous ions, 3) fixation of the removed strontium in

a solid, 4) opportunity for recycling of the waste to attain desired strontium decontamination factors, and 5) elimination of off-gas problems inherent in calcination techniques of waste fixation.

Disadvantages include the probable necessity for filtration of the influent waste after addition of reagents and before passing through the column, and the requirement that this influent be alkaline in pH.

Except on a laboratory scale, no applications of these anion replacement reactions have been made to actual wastes although simulated waste experiments(5) commonly yielded strontium decontamination factors of 10^3 to 10^6.

EXPERIMENTAL WORK

Methods

The experimental apparatus is shown in Figure 1. Influent solutions were passed through Pyrex columns using a Lapp "Microflo" pump calibrated to deliver standardized flow rates through the columns. Temperatures were maintained with blade heaters controlled with a thermoswitch. Influent and effluent solutions were collected and submitted to the Analytical Laboratory of the Hanford Laboratories Operation for radioanalysis. The high-purity Sr^{85}, P^{32}, and C^{14} used in this study were obtained from Oak Ridge National Laboratory. The other chemicals used were of reagent grade in distilled water solutions.

To allow direct comparisons between cation and anion removals, a dimension-less index, C/C_o, was utilized. C_o is the concentration of radioisotope in the influent solution and C is the effluent concentration. Thus $(1-C/C_o)$ (100) equals the per cent removed from solution by the reaction while (C/C_o) (100) equals per cent remaining in solution.

There are no sufficiently long-lived fluorine radioisotopes to use as tracers, which necessitated a different approach for the fluorine removal studies. A large volume (6 liters) of the NaF influent was passed through a calcite column under given experimental conditions. Instead of trying

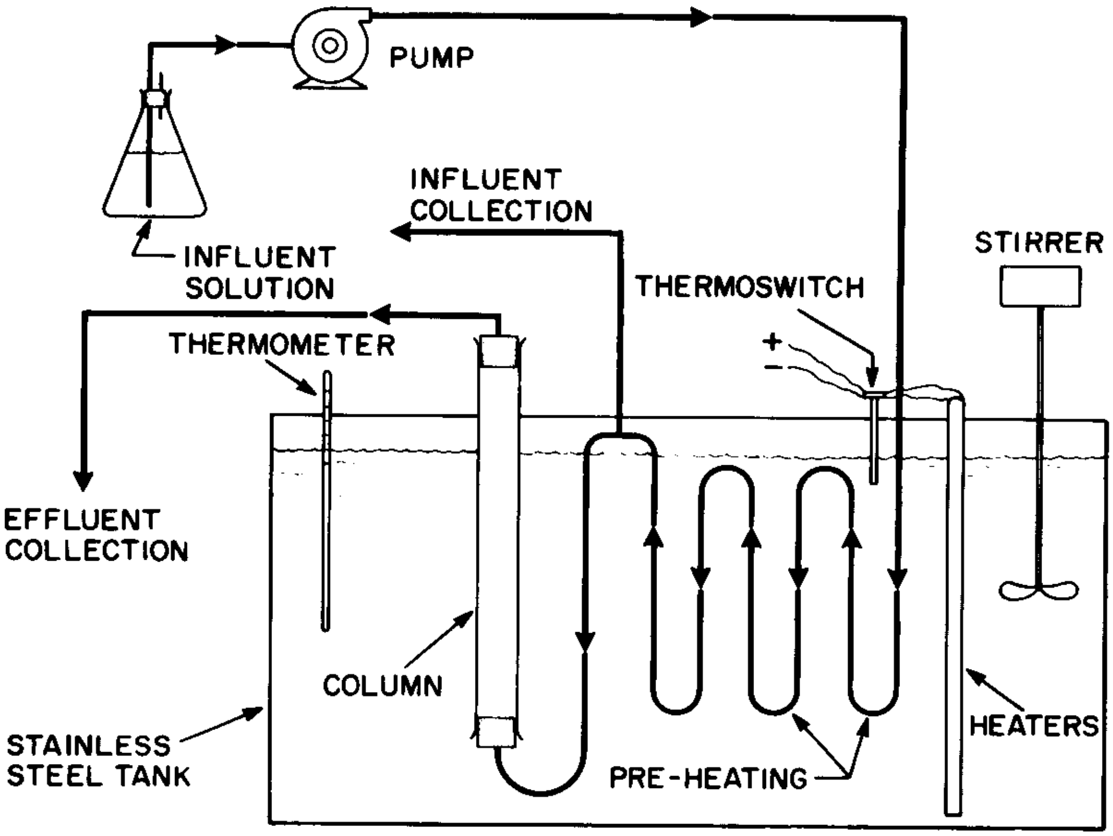

FIGURE 1

Experimental Apparatus

to analyze the effluent solution for fluorine, the amount of CaF_2 in the calcite column at the termination of the run was determined by a modified Berzelius method.(7)

The experimental approach was designed to show the effect of dependent variables (influent pH, flow rate, surface area of the initial solid, temperature, and concentration of the active anion) on the independent variable (C/C_o). "Standard column conditions" were arbitrarily chosen to assure a reasonable reaction rate. These conditions include a temperature of 40 C, an anion concentration of 0.05 M, a flow rate of 410 $ml/cm^2/hr$, an influent pH of 9, an initial surface area of 0.067 m^2/g, and a strontium cation concentration of 0.0063 mg/l. While one of the above-mentioned variables was held at standard column conditions, the others were varied over ranges on both sides of these conditions. This procedure yielded a series of curves that theoretically should have passed through a single point at "standard column conditions." The magnitude of deviation from this point represents total experimental error. Up to ± 10 per cent deviation can result from the compounding of several weighing and measuring errors in obtaining each curve.

Results

Figure 2 shows the effect of the several indicated variables on C/C_o values for F^- in the effluent from a calcite column. Note that the relationship between F^- removal and calcite surface area is approximately linear, i.e., F^- removal is directly proportional to calcite surface area. Doubling the calcite surface area approximately doubles the amount of F^- removed from the system. Also of interest is removal of F^- with influent pH, which increases with decreasing $CaCO_3$ (calcite) stability in the system. Standard conditions are indicated on the various scales by the arrow that cuts across them. The reader should remember that only one variable at a time was changed while the rest were maintained at standard conditions. Figure 3 shows the removal of Sr^{+2} as affected by the indicated variables. Note that the effect on strontium C/C_o values is quite pronounced at the lower flow rates.

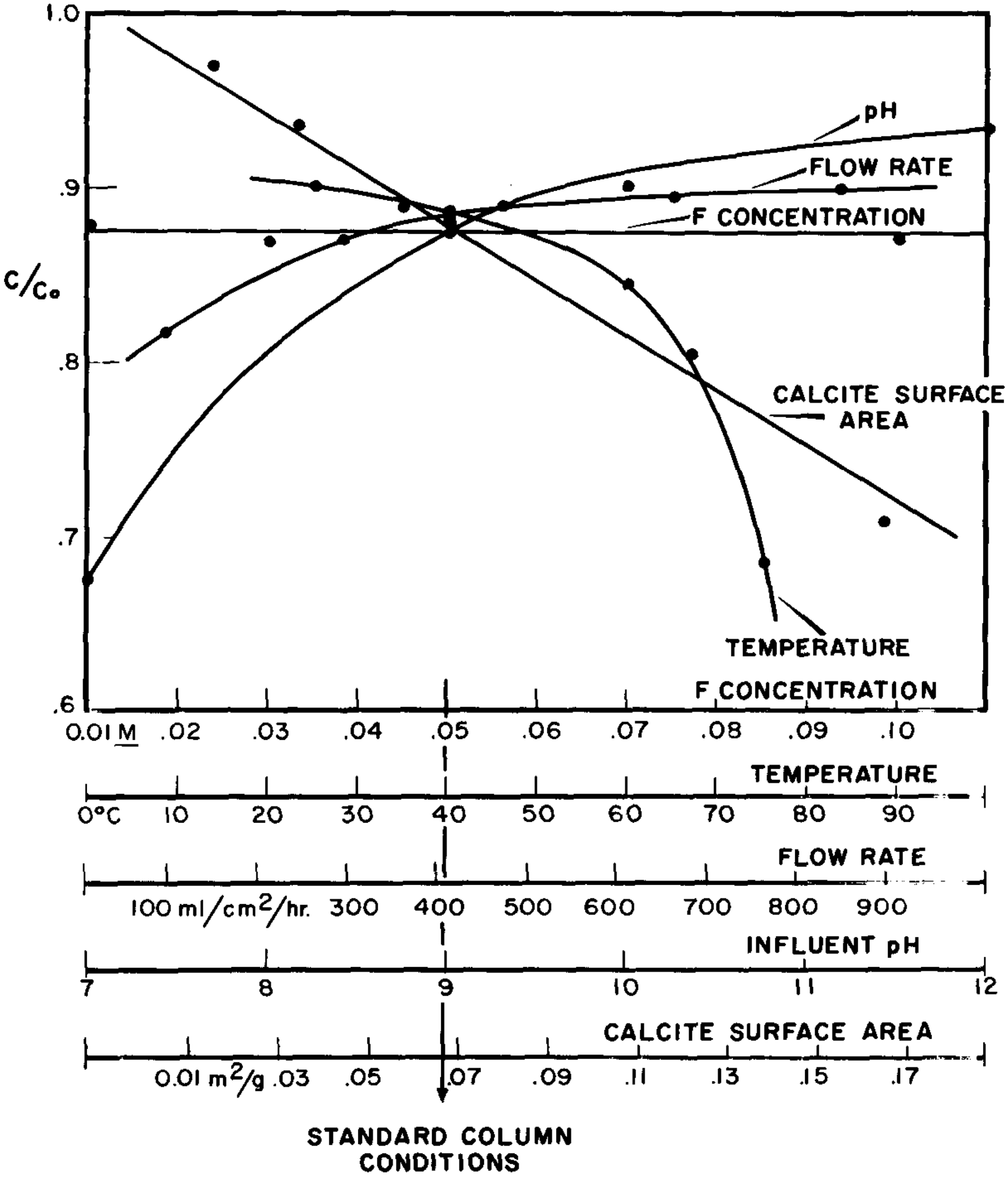

FIGURE 2

Fluoride Removal During Calcite Replacement
by Alkaline, Fluoride-bearing Solutions
Fifty-gram Calcite Columns Were Used to Obtain These Data
All Solutions Contained 1M NaCl in Addition to Their Other Constituents

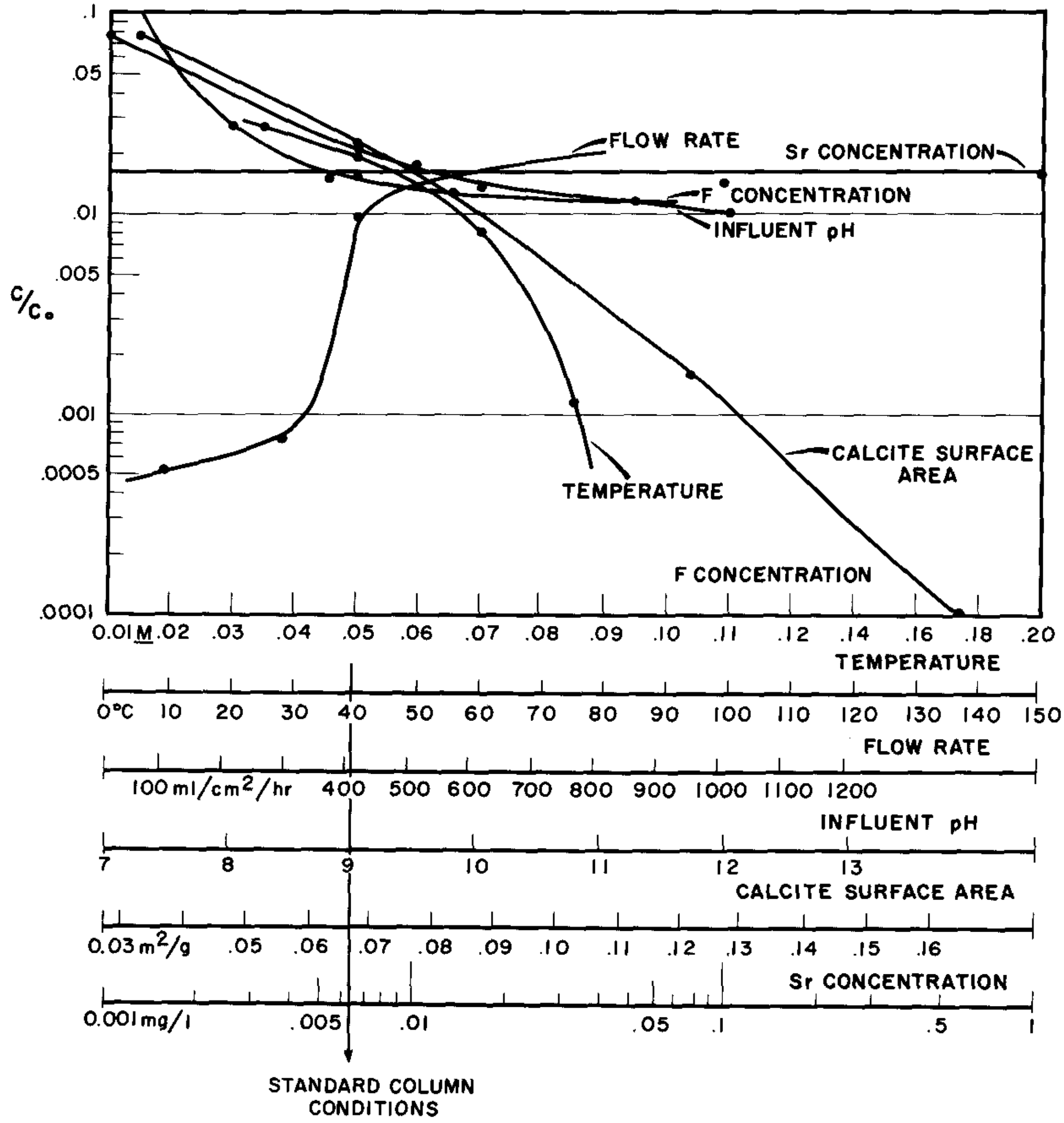

FIGURE 3

Strontium Removal During Calcite Replacement
by Alkaline, Fluoride-bearing Solutions
Fifty-gram Calcite Columns Were Used to Obtain These Data
All Solutions Contained 1M NaCl in Addition to Their Other Constituents

Figure 4 is a photomicrograph of an optical grade calcite rhomb partially replaced by fluorite (CaF_2). This replacement was accomplished by placing a calcite rhomb in a stirred 0.5 M alkaline NaF solution for two weeks and photographing a thin section of the partially replaced calcite by reflected light. Note the well-preserved outline of the original calcite rhomb now composed of CaF_2, and the banded appearance of the CaF_2. This CaF_2 layer is 0.5 mm at its greatest dimension. Much of this outer replacement layer was torn away during grinding and polishing of the thin section, as can be observed in Figures 4 and 5.

The subject of Figure 5, fluorite replacement along a cleavage crack in the original calcite, can be seen in the extreme lower left of Figure 4. A vestigial outline of the original calcite crack can be seen in the resulting fluorite. The fluorite crystals are elongated between the present calcite-fluorite interface and the outline of the original crack. It is obvious from Figure 5 that F^- has diffused down the original calcite crack and CO_3^{-2} back out.

The alteration product was definitely identified as fluorite from X-ray diffraction patterns. The presence of one-molar concentrations of the common anions, nitrate, sulfate and chloride, along with fluoride ions in alkaline solutions, did not significantly affect the $CaCO_3$ replacement by fluorite.

Figures 6 and 7 present data on the reaction of calcite with phosphate containing P^{32} and the concomitant removal of strontium traced with Sr^{85}. This reaction was discussed elsewhere(2, 3, 5) as were the calcite reaction with F^- and concomitant removal of strontium traced with Sr^{85}.(1, 4) Note that all of these solutions were 1 M NaCl in addition to their active constituents.

Figures 8 and 9 give data on the replacement of gypsum by calcite as traced with C^{14}, and concomitant Sr^{+2} removal traced with Sr^{85}. Figure 10, the reaction of gypsum with phosphate containing P^{32}, is included to allow comparison of these P^{32} removal data with those of

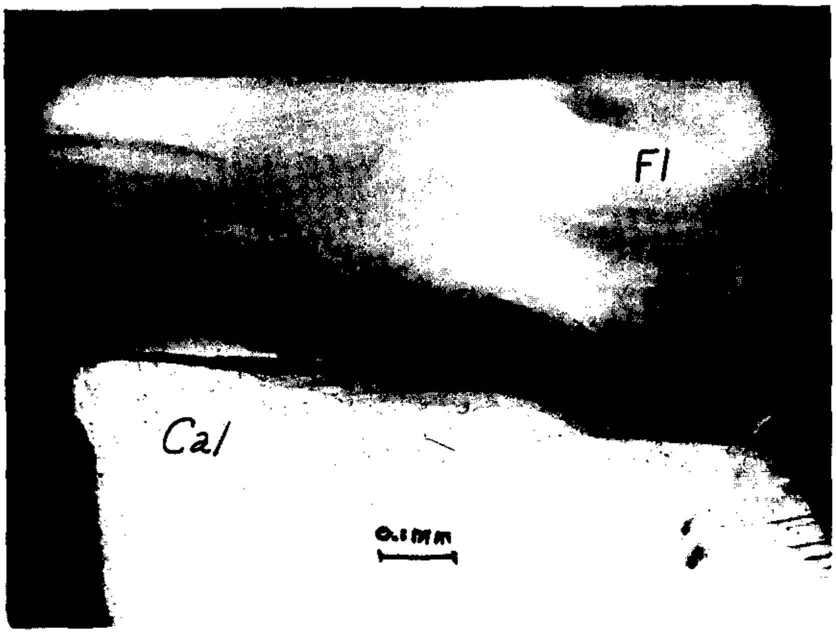

FIGURE 4

A Calcite Rhomb, Sectioned Parallel to $10\bar{1}1$,
Showing the Fluorite Replacement Layer
Cal = Calcite
Fl = Fluorite

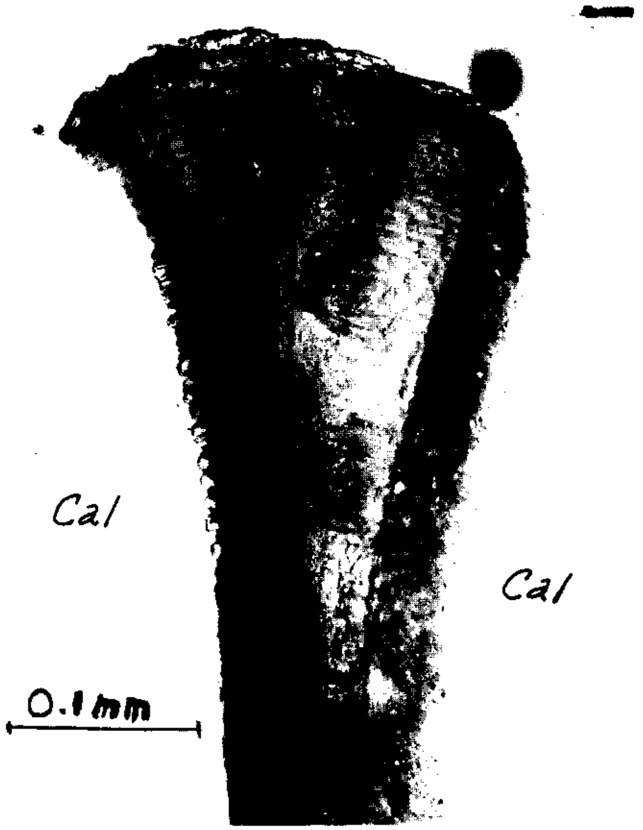

FIGURE 5

Fluorite Replacement of Calcite Along
a Cleavage Crack in the Original Calcite
Cal = Calcite Fl = Fluorite

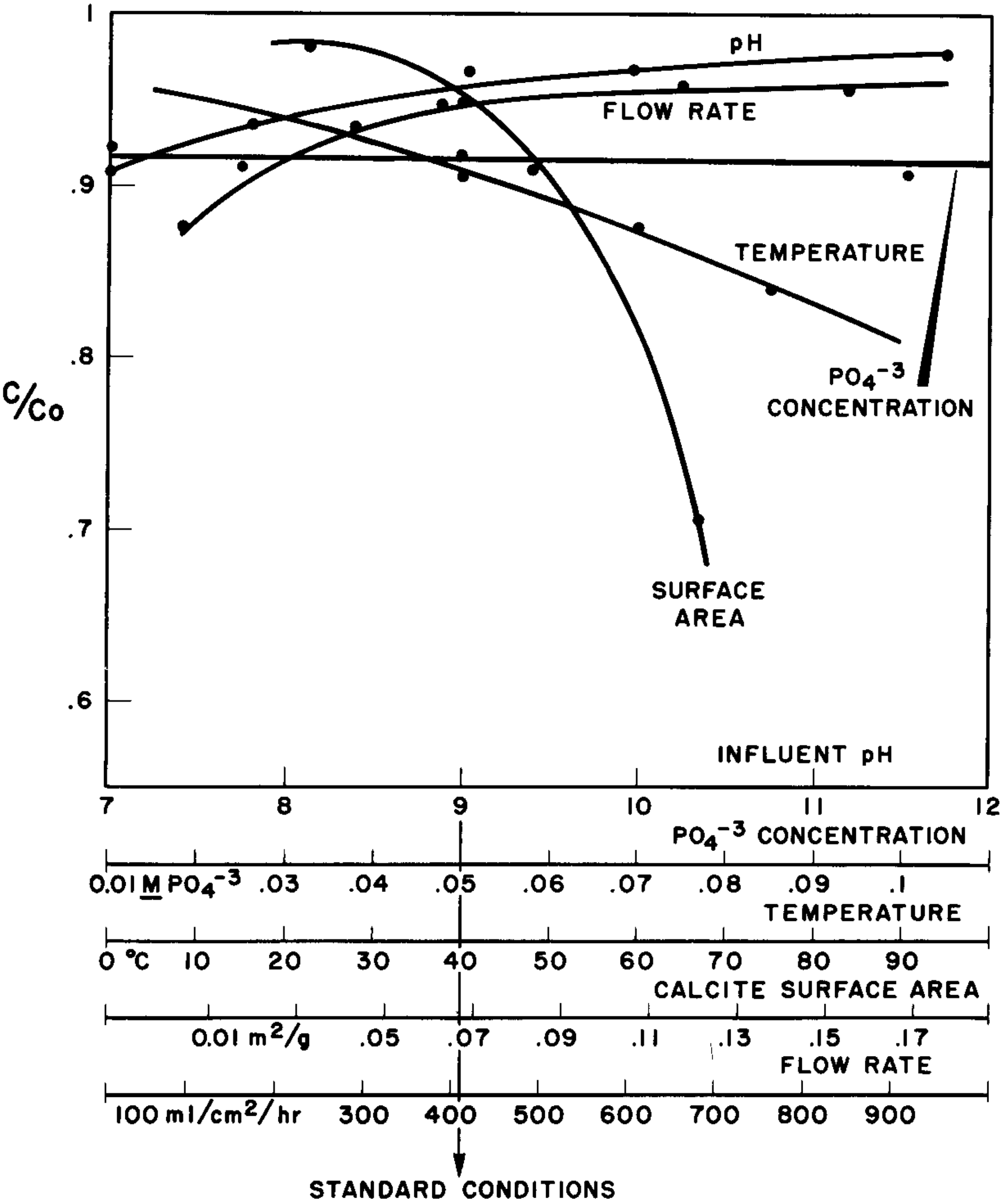

FIGURE 6

Phosphate Removal During Calcite Replacement
by $1\underline{M}$ NaCl, Alkaline, PO_4-bearing Solutions
Fifty-gram Calcite Columns Were Used to Obtain These Data

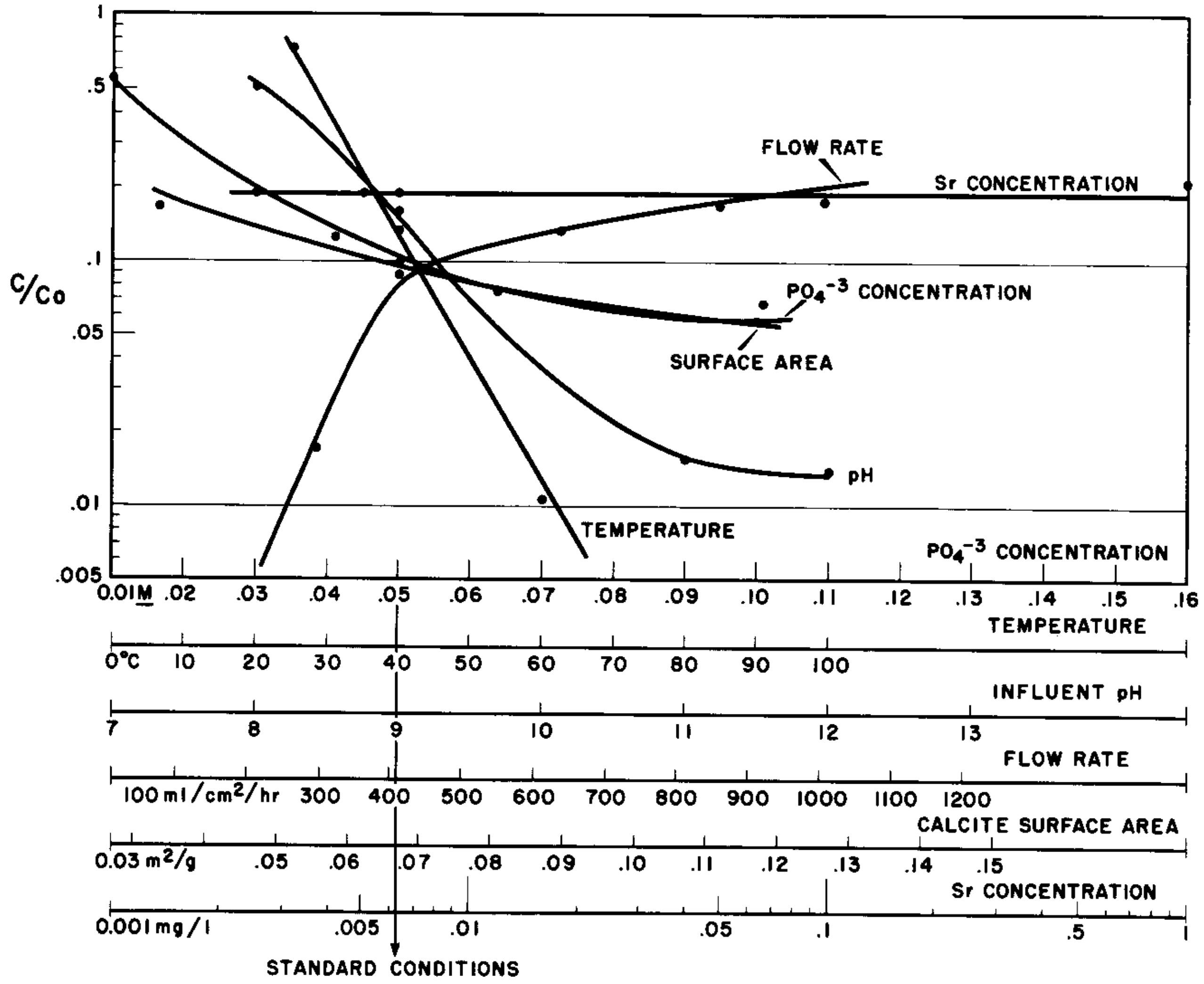

FIGURE 7

Strontium Removal During Calcite Replacement
Fifty-gram Calcite Columns Were Used to Obtain These Data

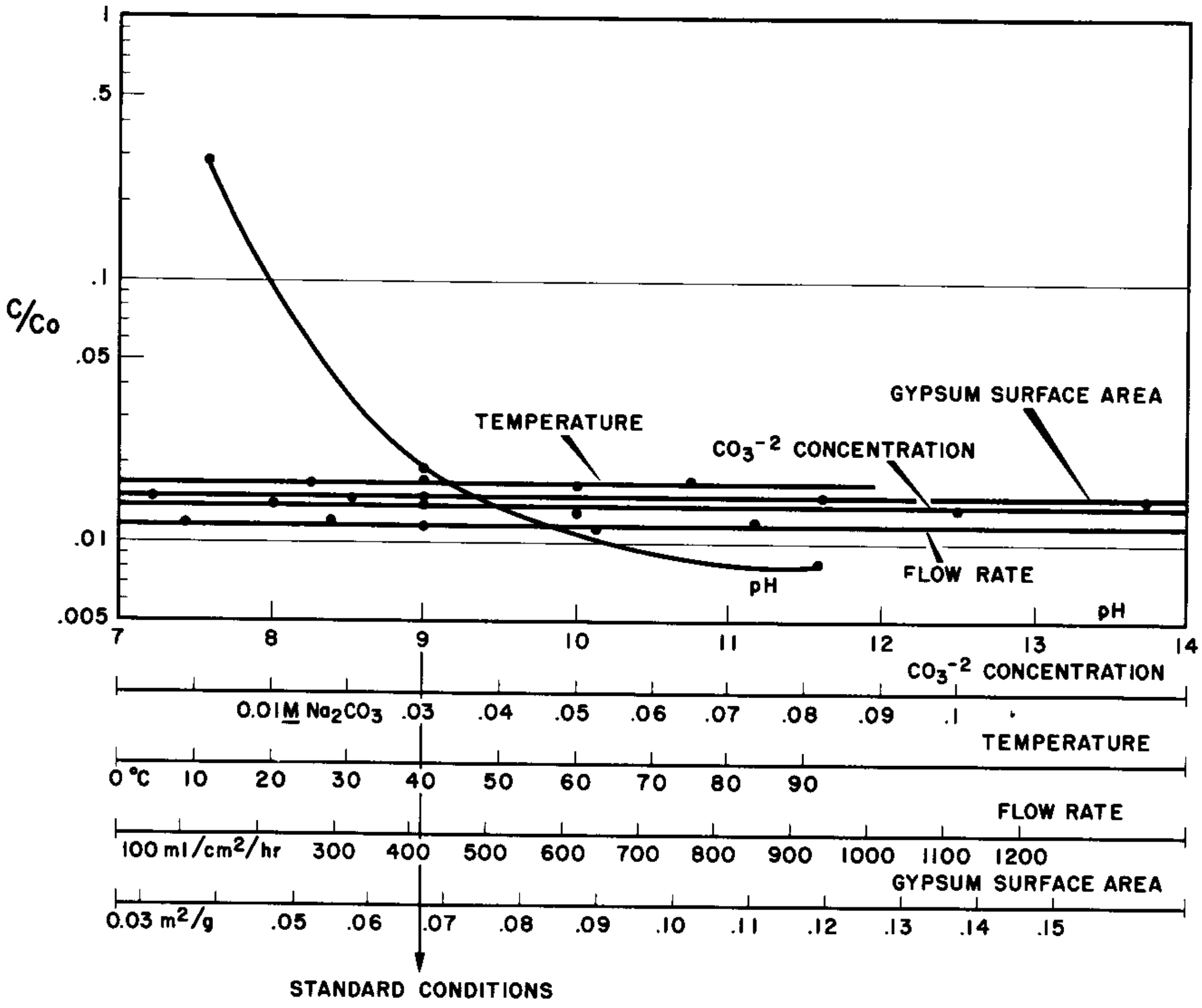

FIGURE 8

Carbonate Removal During Gypsum Replacement by Alkaline, 1M NaCl, CO$_3^{-2}$-bearing Solutions

Fifty-gram Gypsum Columns Were Used to Obtain These Data

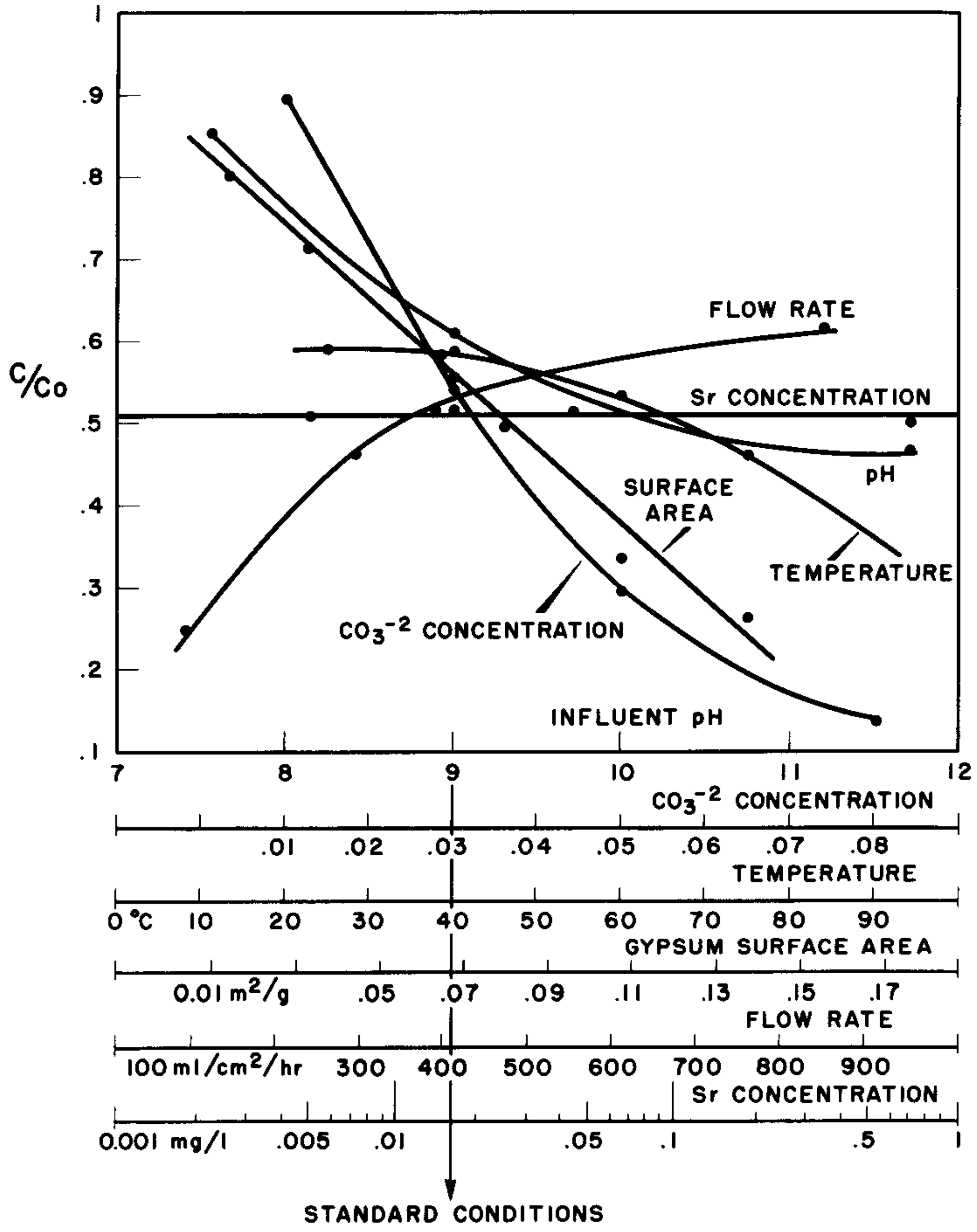

FIGURE 9

Strontium Removal During Gypsum Replacement by Alkaline, $1\underline{M}$ NaCl, CO_3^{-2}-bearing Solutions
Fifty-gram Gypsum Columns Were Used to Obtain These Data

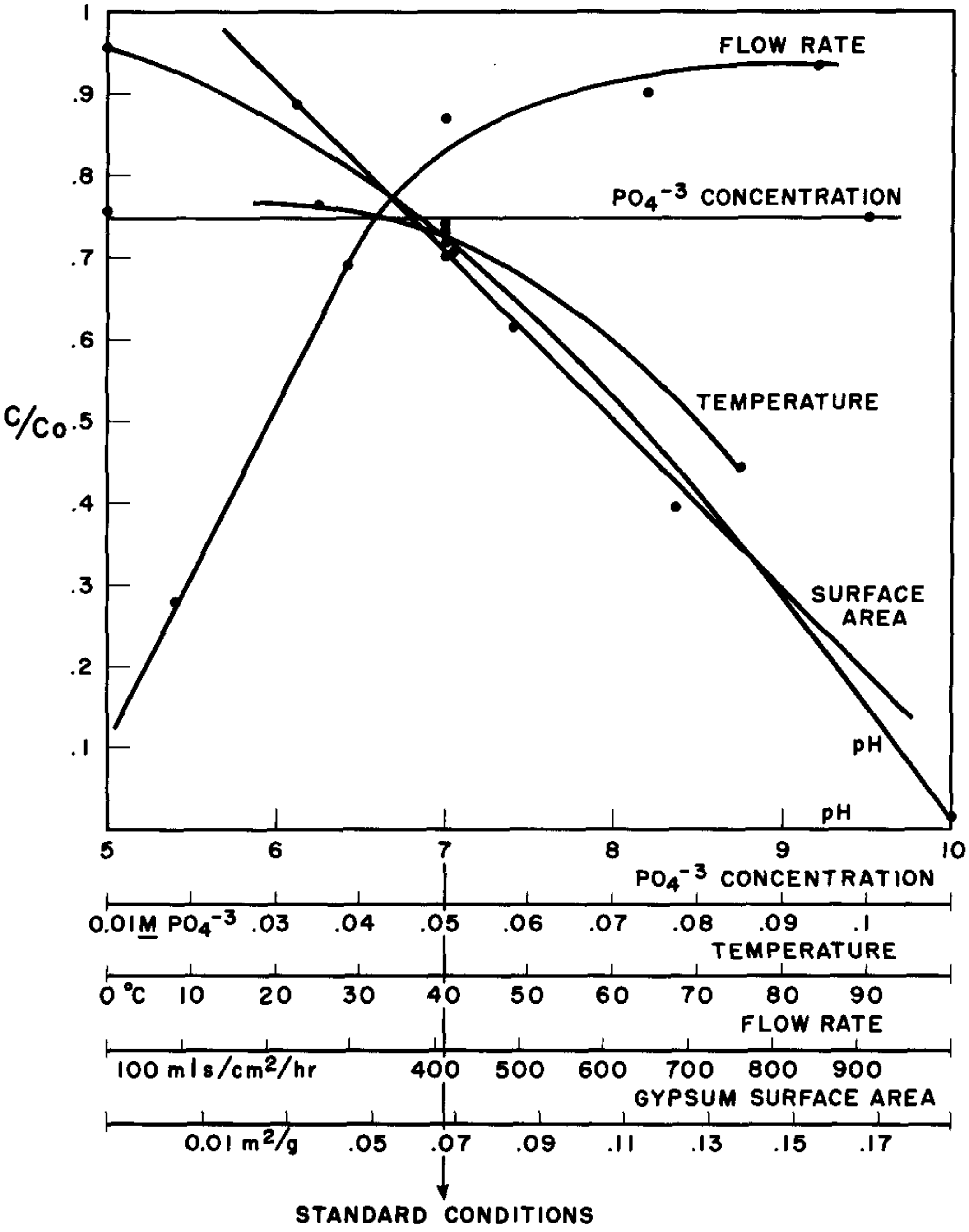

FIGURE 10

Phosphate Removal During Gypsum Replacement by Alkaline, 1M NaCl, PO_4^{-3}-bearing Solutions
Fifty-gram Gypsum Columns Were Used to Obtain These Data

calcite in Figure 6. Note, though, that standard conditions include a pH of seven with gypsum but a pH of nine with calcite and are thus not directly comparable.

Figure 11 shows a photomicrograph of an apatite layer formed on an optical grade calcite rhomb by immersion of the calcite in a 0.1 M Na_3PO_4 solution for two weeks.

Figure 12 is a photomicrograph of a former single crystal of gypsum completely replaced with calcite by immersion in a 0.2M Na_2CO_3 solution for two weeks. The apparent volume reduction may be due to material removed during cutting and grinding of this section.

Several experiments were completed in the kinetic system calcite-Na^2CO_3 - Na_2SO_4 - NaF - Na_3PO_4. The results of these experiments are presented in Table I. The final products in all cases were identified by X-ray diffraction. Note that one obtains a final product, not a mixture of final products. The same experimental apparatus as shown in Figure 1 was used to obtain these results.

Data Treatment

Several variables will affect the difference in solubility between original and final product including active anion concentration, extraneous ion concentrations, temperature and pH. With systems containing hydroxyl and carbonate compounds, we may assume that solution pH would have a significant effect on this solubility difference. Figure 13 is a comparison of several anion replacement reactions under comparable conditions. Note that the specific reaction rates for calcite-phosphate and calcite-fluoride are decreasing respectively with increasing pH. This divergence with increasing pH is interpreted as a decreasing difference between the solubility of calcite and fluorite, and between the solubility of calcite and apatite. The difference in solubility between gypsum and calcite or apatite, on the other hand, increases with increasing pH, as do the gypsum-carbonate and gypsum-phosphate reaction rates.

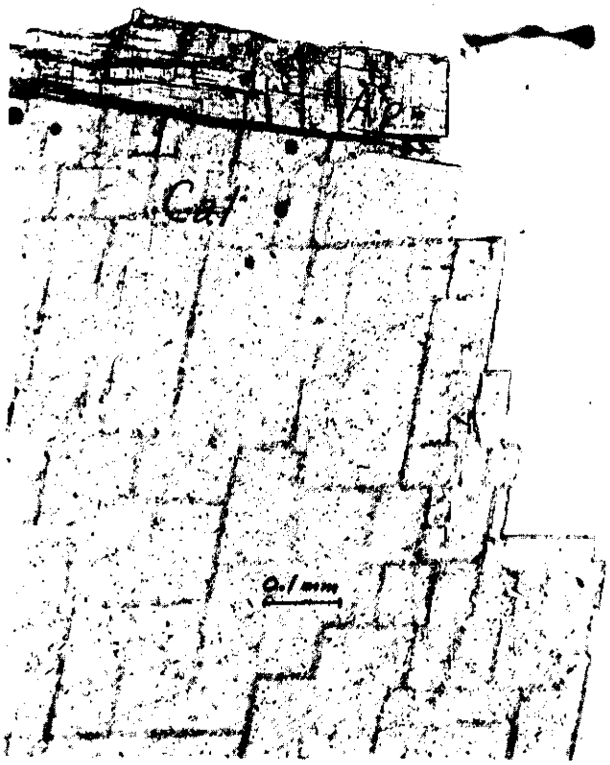

FIGURE 11

Photomicrograph of a Calcite Rhomb and Attached Apatite Replacement Layer
Ap = Apatite
Cal = Calcite

AEC-GE RICHLAND, WASH.

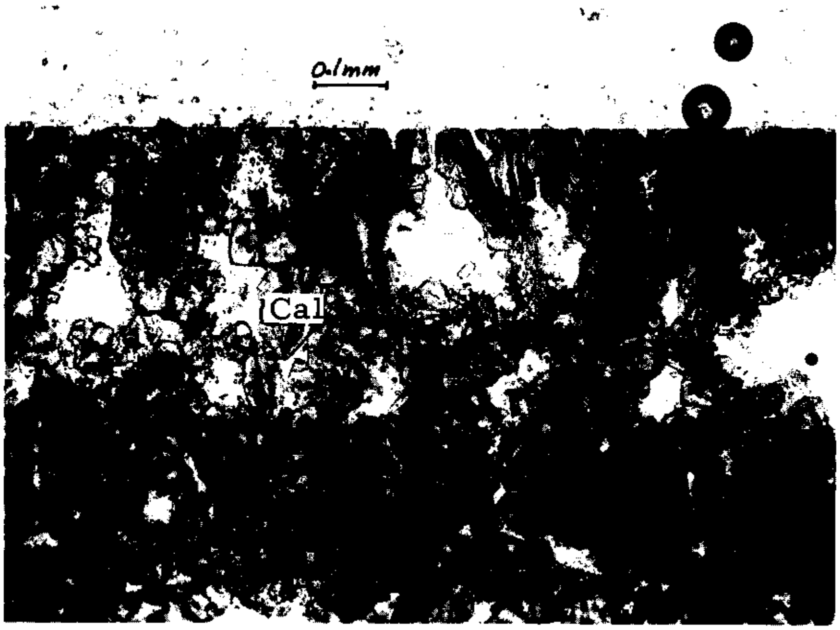

FIGURE 12

Photomicrograph of a Former Single Gypsum Crystal
Completely Replaced by Calcite
The Straight Line at the Top of the Photo Represents
the Original Gypsum Crystal Outline
Cal = Calcite

TABLE I

KINETIC PHASE RELATIONS IN SOME CALCIUM-ANION SYSTEMS AS AFFECTED BY pH

Influent Solution	Influent pH	Effluent pH	Column Material	Final Product
0.03 $\underline{M}$ Na_2SO_4	3.1	6.6	Calcite	Calcite
0.03 $\underline{M}$ Na_2CO_3	10.9	10.8	Fluorite	Calcite
0.03 $\underline{M}$ Na_2SO_4	4.2	4.1	Fluorite	Fluorite
0.03 $\underline{M}$ Na_2SO_4	4.2	4.2	Apatite	Gypsum
0.03 $\underline{M}$ Na_2CO_3 0.03 $\underline{M}$ Na_2SO_4	4.1	6.5	Calcite	Calcite
0.03 $\underline{M}$ Na_2SO_4 0.03 $\underline{M}$ Na_2SO_4	9.2	9.2	Calcite	Calcite
0.03 $\underline{M}$ NaF 0.03 $\underline{M}$ Na_2CO_3	7.2	8.6	Calcite	Fluorite
0.03 $\underline{M}$ NaF 0.03 $\underline{M}$ Na_2CO_3	9.6	9.8	Calcite	Fluorite
0.03 $\underline{M}$ NaF 0.03 $\underline{M}$ Na_2CO_3	7.1	7.2	Gypsum	Fluorite
0.03 $\underline{M}$ NaF 0.03 $\underline{M}$ Na_2SO_4 0.03 $\underline{M}$ Na_2CO_3	9.3	9.7	Calcite	Fluorite
0.03 $\underline{M}$ NaF 0.03 $\underline{M}$ Na_2SO_4 0.03 $\underline{M}$ Na_2CO_3	9.2	9.2	Fluorite	Fluorite
0.03 $\underline{M}$ NaF 0.03 $\underline{M}$ Na_2SO_4 0.03 $\underline{M}$ Na_2CO_3 0.03 $\underline{M}$ Na_3PO_4	11.8	11.7	Calcite	Apatite
0.03 $\underline{M}$ NaF 0.03 $\underline{M}$ Na_2SO_4 0.03 $\underline{M}$ Na_2CO_3 0.03 $\underline{M}$ Na_3PO_4	7.2	7.4	Calcite	Apatite
0.03 $\underline{M}$ NaF 0.03 $\underline{M}$ Na_2SO_4 0.03 $\underline{M}$ Na_2CO_3 0.03 $\underline{M}$ Na_3PO_4	4.2	6.5	Calcite	Fluorite

The data of Table I were obtained by passing the influent solutions through two centimeter diameter chromatographic tubes containing three grams of reagent grade initial column material at 60 C.

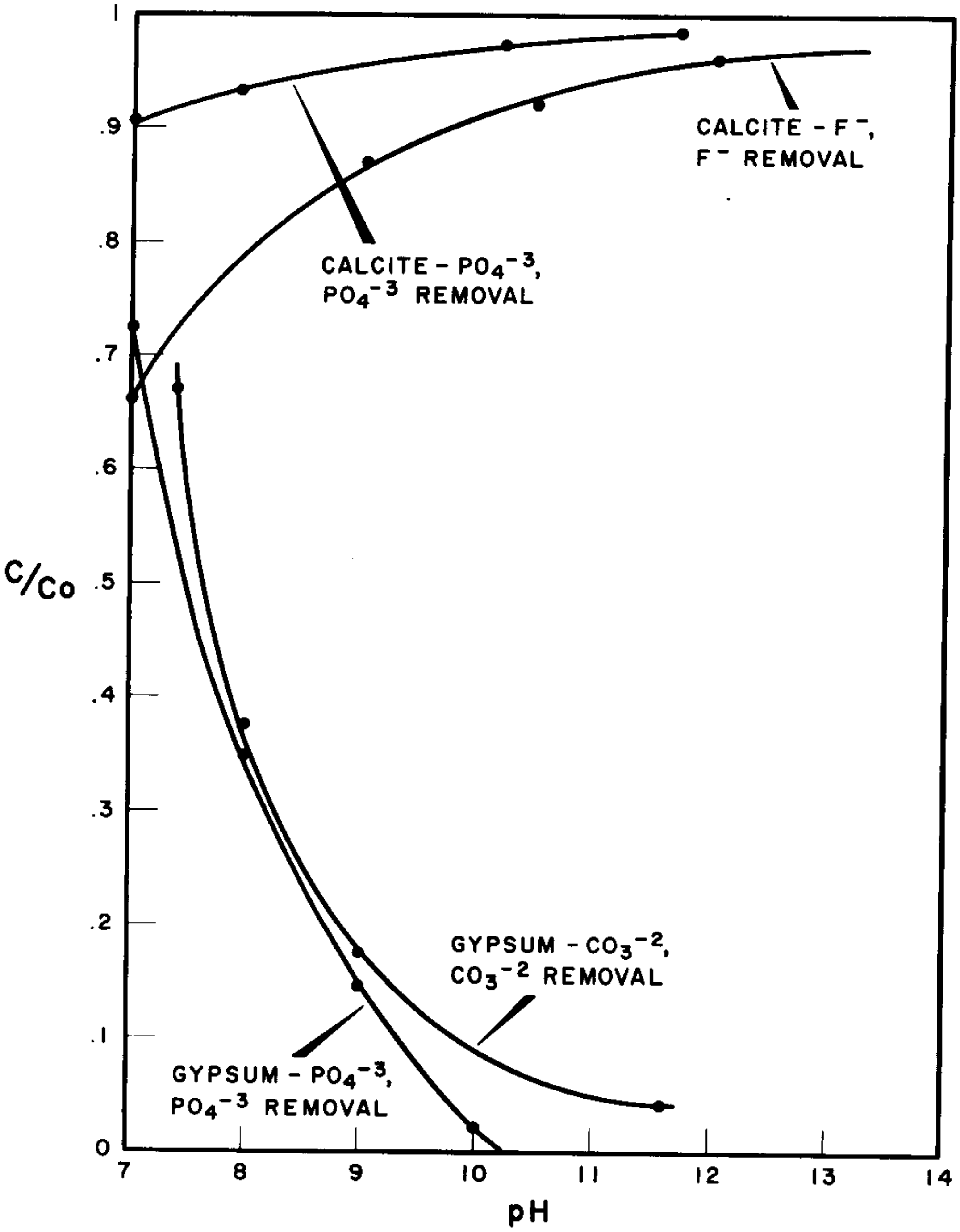

FIGURE 13

The Rate of Anion Removal During
Anion Replacement Reactions as Affected by pH
Data from Figures 2, 6, 8 and 10

These solubility differences can be approximated by the relative amounts of common cation (Ca^{+2}) that each (initial solid and final product) releases into solution under given equilibrium conditions. With solutions 0.03 $\underline{M}$ NaF, 0.03 $\underline{M}$ Na_2SO_4, 0.03 $\underline{M}$ Na_2CO_3 and 0.03 $\underline{M}$ Na_3PO_4 passed through a column containing an initial solid we can infer which final solid is stable at several pH values. The computation for CaF_2 is straightforward. Assuming the HF completely ionized, we may use the activity product constant for CaF_2 equal to 1.7×10^{-10}.(8) Given that $[F^-]$ equals 0.03 $\underline{M}$, the concentration of Ca^{+2} at 25 C is 1.89×10^{-7} $\underline{M}$. The computation for gypsum is likewise unaffected by $[H^+]$ above pH 3, and with a gypsum activity product constant equal to 4.57×10^{-5},(8) yields a $[Ca^{+2}]$ of 1.52×10^{-3} $\underline{M}$ in 0.03 $\underline{M}$ Na_2SO_4 at 25 C. With calcite, $[CO_3]_T$, or total carbonate, does not equal $[CO_3^{-2}]$. Therefore, we must use the relationship(6)

$$[CO_3^{-2}] = \frac{[CO_3]_T}{\frac{[H^+]^2}{K_{12}K_1} + \frac{[H^+]}{K_1} + 1}$$

where:

$[CO_3]_T$ = total carbonate

= 0.03 $\underline{M}$

K_1 = HCO_3^- dissociation constant

$$= \frac{[CO_3^{-2}][H^+]}{[HCO_3^-]}$$

= 6.02×10^{-11},(10)

and

$$K_{12} = H_2CO_3 \text{ dissociation constant}$$

$$= \frac{\left[HCO_3^-\right]\left[H^+\right]}{\left[H_2CO_3\right]}$$

$$= 4.46 \times 10^{-7}.^{(10)}$$

Thus at pH 7 and 25 C,

$$\left[CO_3^{-2}\right] = \frac{3 \times 10^{-2}}{\frac{(1 \times 10^{-7})^2}{(6.02 \times 10^{-11})\ (4.46 \times 10^{-7})} + \frac{(1 \times 10^{-7})}{(6.02 \times 10^{-11})} + 1} = \frac{0.03}{2033} =$$

$$1.48 \times 10^{-5} \underline{M}\ CO_3^{-2}.$$

Using an activity product constant of 4.68×10^{-9} for calcite$^{(8)}$

$$\frac{4.68 \times 10^{-9}}{1.48 \times 10^{-5}} = 3.16 \times 10^{-4} \underline{M}\ Ca^{+2}$$

At pH 12 and 25 C,

$$\left[CO_3^{-2}\right] = \frac{3 \times 10^{-2}}{\frac{(1 \times 10^{-24})}{(6.02 \times 10^{-11})\ (4.46 \times 10^{-7})} + \frac{(1 \times 10^{-12})}{(6.02 \times 10^{-11})} + 1} = \frac{0.03}{1.0166} =$$

$$2.95 \times 10^{-2} \underline{M}\ CO_3^{-2}.$$

and

$$\frac{4.68 \times 10^{-9}}{2.95 \times 10^{-2}} = 1.59 \times 10^{-7} \underline{M}\ Ca^{+2}$$

Figure 14 is a graph of these data. The activity product constants used here$^{(8)}$ are evidently not applicable to these systems or the curve for fluorite would not overlap that of calcite. The general relationships are valid, however. Apatite could not be included because of uncertain

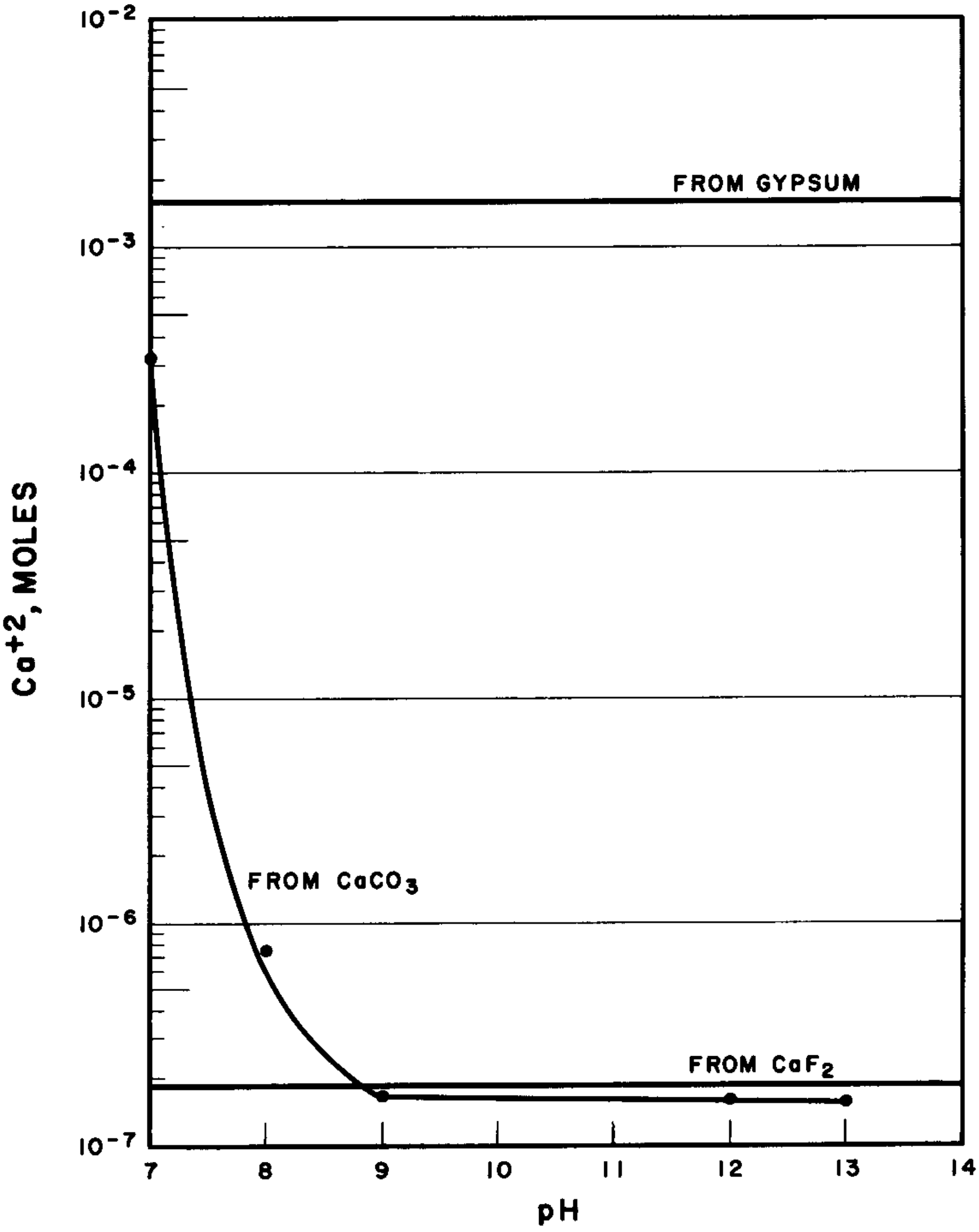

FIGURE 14

Relative Amounts of Ca^{+2}
from Several Compounds in Equilibrium With
Indicated 0.03 M SO_4^{-2}, CO_3^{-2} and F^- Solutions at Various H^+ Concentrations

composition, and therefore solubility data. However, apatite does replace calcite in preference to fluorite at higher pH. We may conclude that the curve for apatite falls below that of fluorite above pH 7.

Figure 15 shows the removal of Sr^{+2} during the replacement reactions of Figure 13. Note that unlike the anion removals in Figure 13, Sr^{+2} removal always increases with increasing pH, probably due to a tendency toward decreasing hydroxide solubility. Ce^{+3} also exhibited increased removal with increased pH, suggesting that the phenomenon is common to all cations removed during anion replacement reactions.

CONCLUSIONS

These data support the premise that only one reaction product is stable in a given system. Moreover, the rate of formation of this stable reaction product is directly proportional to the magnitude of the solubility difference between the initial and final solids. More than one final product indicates that the reaction has not been completed, or the initial solid was a mixture of compounds, one of which was less soluble in the system than any possible reaction product.

The effect of the crystal structure of the final product on Sr^{+2} removal is even more evident than pH on anion removal rates. The crystal lattices of SrF_2 and CaF_2 are both of the fluorite type, while Ca-apatite and Sr-apatite are also of the same structural types. $SrCO_3$, on the other hand, is an aragonite type structure while calcite is not. This difference in lattice types inhibits the removal of Sr^{+2} during the replacement of gypsum by carbonate-bearing solutions. However, all other things being equal, the rate of concomitant Sr^{+2} removal into the lattice of the final product always increased with increasing pH.

The effect of the various reaction variables on strontium removal rate was additive, i.e., the effect of given pH change on the strontium removal rate and the effect caused by a given temperature change could be summed to give the additive effect on strontium removal rate when both the pH and temperature changes were made sumultaneously.

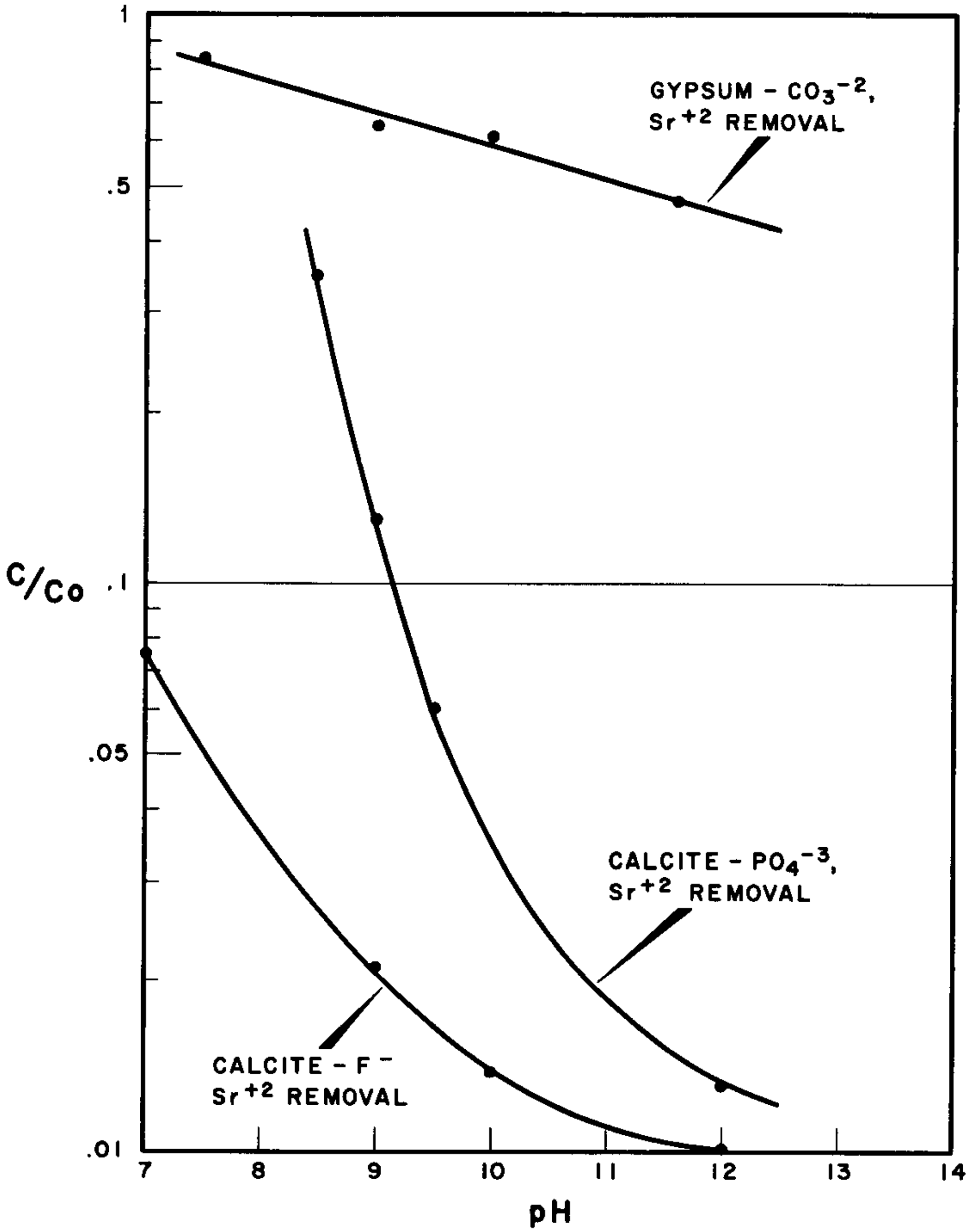

FIGURE 15

Concomitant Removal of Strontium into
the Final Reaction Product as Affected by pH
Data from Figures 3, 7 and 9

Only the application of these replacement reactions to column use was considered here. One advantage accruing to the use of columns for these reactions is the large volume reduction of contaminated material. On the order of several thousand column volumes can be passed through these columns before the initial column material is completely reacted and thus no longer will remove strontium from the waste solution. Furthermore the strontium can be removed from wastes containing large concentrations of extraneous cations and the effluent solution can be recycled to attain the desired strontium decontamination factors. Fixation of the removed strontium in a solid is assured along with elimination of off-gas problems inherent in calcination techniques. Certain restrictions are imposed on the types of wastes that may be decontaminated by these replacement reactions due to the necessity for the influent solution to be alkaline in pH and contain the necessary reagent. It is highly probable that a filtration or settling step must be included after the influent solution is made alkaline and the reagent added, and before passage through the column. Otherwise any radioisotope-containing precipitates will pass through the column undecontaminated.

It should be emphasized that only simulated radioactive wastes, usually containing a single radioisotope, were used in mineral replacement reaction experiments on a laboratory scale. No actual radioactive waste applications have been made on any scale. However, strontium decontamination factors of 10^3 to 10^6 from simulated high-salt waste were commonly encountered during these laboratory studies. There is every reason to believe, in the author's opinion, that these mineral replacement reactions can be successfully adapted to the removal of radiostrontium from actual radioactive wastes.

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