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THE METASOMATIC REPLACEMENT OF LIMESTONES
ALKALINE, FLUORIDE-BEARING SOLUTIONS

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L. L. Ames, Jr.*

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HW SA-1759

THE METASOMATIC REPLACEMENT OF LIMESTONES BY ALKALINE, FLUORIDE-BEARING SOLUTIONS

L. L. Ames, Jr.*

ABSTRACT

A laboratory study of the kinetics of limestone replacement by alkaline, fluoride-bearing solutions is presented. Data on the effects of temperature, concentration (fluoride ion and cations), pH, calcite surface area, and flow rates on fluoride ion, Sr^{+2}, Ce^{+3}, and U^{VI} removal are included. These data are discussed in relation to field occurrences of fluorite replacement deposits.

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INTRODUCTION AND PREVIOUS WORK

During a study of the replacement of limestone by phosphorite (Ames, in press) fluorine was added to the alkaline limestone-altering solution as NaF. It was determined that the presence of F did not appreciably affect the rate of formation of apatite, and also led to the discovery that alkaline, fluoride-bearing solutions, in the absence of PO_4^{-3}, can readily alter limestone to fluorite at 25°C and one atmosphere of pressure. A literature search revealed that Grayson (1956) previously reported the acid reaction of HF with calcite. This paper presents a portion of the study of the fluoride-calcite replacement reaction in alkaline systems and the inclusion of U^{VI}, Sr^{+2}, and Ce^{+3} within the fluorite lattice during this reaction.

Garrels and Dreyer (1952) and Holser (1947) discussed metasomatic replacement ore deposits in general, the former authors by studying replacement of limestone with supergene copper minerals. McKinstry (1955) discussed the criteria of, and some reasons for, the occurrence of limestone replacement deposits.

The replacement of limestones by fluorite has been known for some time. Many authors have previously reported field occurrences of fluoride metasomatism (Currier, 1937, 1944, Gillerman, 1953, Grogan, 1949, Heinrich, 1958, Ladoo and Myers, 1951, Lovering, 1954, Peters, 1958, Staatz and Osterwald, 1956, Thurston et al., 1954, Wilmarth et al., 1952, and Weller et al, 1952). Most of these authors either directly postulated that acid replacing solutions containing HF reacted with the limestone to form fluorite, or alluded to this reaction. Weller et al. (1952) were the only authors to conclude that the fluorite-forming solutions must have been neutral to alkaline. Sahama (1945) reported in a thermochemical study of the stability relations between fluorite, sellaite, and dolomite that both fluorite and sellaite are stable in dolomite at low temperatures.

Peters (1958) mentioned the reversibility of the reaction between fluoride solutions and limestone as a probable explanation for the corrosion or removal of existing fluorite.

The occurrence of minor amounts of various cations in fluorite including the rare earths, Sr and U, was previously known (Bray, 1942, Goldschmidt, 1954, Rankama and Sahama, 1950, Dana, 1951, Heinrich, 1958, Peters, 1956, Staatz and Osterwald, 1956). It was postulated by Heinrich (1958), Green and Kerr (1953), and Staatz and Osterwald (1956) that U^{IV} was substituting for $2Ca^{+2}$ within the crystal lattice of uraniferous fluorite. Weyl (1951), on the other hand, reported that U^{VI} could substitute for Ca^{+2} in CaF_2 if four fluoride ions in the neighborhood of the U^{VI} were replaced by four oxygen ions. These uraniferous fluorite deposits included the Thomas Range, Utah (Staatz and Osterwald, 1956, Thurston, et al., 1954) where uraniferous fluorite occurs in pipes replacing a dolomite, the Daisy fluorite mine near Beatty, Nevada (Lovering, 1954), the Monarch deposit in Beaver County, Utah (Thurston, et al., 1954), the Eagle Mountains, Texas deposit (Gillerman, 1953), and the Marysvale, Utah deposit (Green and Kerr, 1953).

Gableman (1955) pointed out the relationship between temperature of formation and U content of Western United States fluorites. The radioactive fluorite deposits were characterized as low-epithermal while the non-radioactive fluorites were high-epithermal.

METHODS OF INVESTIGATION

The experimental equipment is shown in Figure 1. Prepared influent solutions were passed through standard Pyrex columns by a Lapp "Microflo" pump calibrated to deliver standardized flow rates through the calcite 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. Calcite surface area determinations and chemical analysis were by the same laboratory. The high-purity Sr^{85} and Ce^{144} used in this study were obtained from Oak Ridge, and the uranyl nitrate was a Hanford product. The other chemicals used were of reagent grade in distilled water solutions. There are no sufficiently long-lived F radioisotopes to use as tracers, which necessitated a different approach for the F removal studies.

A large volume (6 liters) of the NaF influent was passed through a calcite column under given experimental conditions. Instead of trying to analyze the effluent solution for F, the amount of CaF_2 in the calcite column at the termination of the run was determined by a modified Berzelius method (Hillebrand, 1953).

To allow direct comparisons between cation and anion removals, a dimensionless index, C/C_o, is utilized. C_o is the influent radioisotope or F concentration 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 several independent variables in a kinetic system of this type. These include flow rate, pH, temperature, calcite surface area, F concentration, and Ce^{+3}, Sr^{+2}, or U^{VI} concentration. To completely study this system, a factorial design would be required (Gore, 1949). Taking four points on each of six variables (pH = 7, 9, 11, 13; F = 0.1, 0.05, 0.03, 0.01M, etc.) would necessitate

$(4)^6$ separate experiments. The experimental approach actually utilized here was not factorial, but was designed to yield trends between dependent and independent variables that would be comparable in their effect on F^-, U^{VI}, Sr^{+2}, and Ce^{+3} removal.

"Standard conditions" were arbitrararily chosen that assured a reasonable reaction rate. While five of the abovementioned variables were held at these standard conditions, the sixth was varied over ranges on both sides of the standard conditions (Figures 3, 4, and 5). This procedure yielded a series of six curves that theoretically passed through a single point at "standard conditions."

Thus one may directly compare the data of Figures 2, 3, 4, and 5, except for the concentrations of the specific radioisotopes with that of F removal.

RESULTS

Table 1 gives a partial chemical analysis of the relatively pure calcite utilized in this study.

TABLE 1. PARTIAL CHEMICAL ANALYSIS OF THE CALCITE USED IN THIS STUDY

Constituent	Weight per cent
CaO	52.90
CO_2	43.40
SiO_2	1.00
MgO	1.96
SrO	0.83
Total Fe	0.01
Al_2O_3	0.22
H_2O^+	0.16
Total	100.48

Plate 1 is a photomicrograph of an optical grade calcite rhomb partially replaced by fluorite. This replacement was accomplished by placing a calcite rhomb in a stirred, 0.5<u>M</u> 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 Plate 1 and Plate 2.

The subject of Plate 2, fluorite replacement along a cleavage crack in the original calcite, can be seen in the extreme lower left of Plate 1. 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 Plate 2 that F^- has diffused down the original calcite crack and CO_3^{-2} back out. It is quite likely that this material transfer was intercrystalline. One cannot explain the high replacement rate if the material transfer took place via any other route (intracrystalline).

The alteration product was definitely identified as fluorite from X-ray diffraction patterns. The presence of one-molar concentrations of the common anions NO_3^-, SO_4^{-2} and Cl^- along with fluoride ions in alkaline solutions did not significantly affect the $CaCO_3$ replacement by fluoride. On the other hand, the presence of PO_4^{-3} with fluoride ions always caused the formation of apatite (rather than fluorite) as the reaction product at alkaline pH.

Because several fluorite replacement deposits are known to occur in dolomite, a portion of the dolomite-magnesite-NaF system was examined. Sellaite did not occur as a replacement product of dolomite or magnesite under the experimental conditions of this study. Fluorite was the only stable fluoride up to 60°C, 0.5M NaF, and one atmosphere of pressure

The passage of a 0.5M $NaHCO_3$ solution through a 10g column of reagent grade CaF_2 yielded an initial $CaCO_3$ that was rapidly dissolved in the same solution as the bicarbonate.

Figure 2 shows the effect of the several indicated variables on C/C_o values for F. Note that the relationship between F removal and calcite surface area is approximately linear and directly proportional. 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 $CaCO_3$ 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. The failure of these curves to intersect at a single point represents the effects of experimental error. The magnitude of this deviation from the single theoretical point is an indication of magnitude of experimental error.

Figure 3 illustrates the effects of the several variables on C/C_o values for U^{VI} removal. The state of the uranium in this system was previously studied by McKelvey, Everhart, and Garrels (1957) and there is little doubt that the uranium is present as U^{VI} as specified. Here the C/C_o values rise with increasing temperature as contrasted with the comparable behavior of the other cations studied. Calcite surface area and influent flow rates have less effect than with some of the other cations.

Figure 4 gives the effects of the several indicated variables on Ce^{+3} C/C_c values. Note that these values are, on the average, considerably less than the corresponding values of U^{VI} or F. The falling C/C_o value for increasing Ce concentration is probably due to the precipitation of increasing increments of $Ce(OH)_3$ which effectively removes this Ce^{+3} from the kinetic system.

Figure 5 shows the removal of Sr^{+2} as affected by the indicated variables. Note that the effect on Sr C/C_o values is quite pronounced at the lower flow rates.

DISCUSSION

It is evident that acidic ($< pH\ 7.0$) fluorine-bearing solutions are not required to replace limestones and dolomites with fluorite. Experimental results indicated that the altering solution must be alkaline to avoid violent evolution of CO_2. A CO_3^{-2}-rich influent solution replaced the fluoride with carbonate and may either result in a calcite deposit or complete removal of the calcite in solution.

The phenomenon of increased cation removal and decreased anion removal with rising pH was encountered as reported previously by Ames (in press) when PO_4^{-3} was the active anion.

Diffusion of anions to and from the reaction interface is rate-determining and independent of the diffusion rate of U^{VI}, Sr^{+2}, and Ce^{+3}. Diffusion in this instance is considered to be intercrystalline, i.e., the anions move between the resulting fluorite crystals to the reaction interface and back out as postulated by Holser (1947). The crystallites formed by this reaction are very small (Plate 1), and there is no necessity to postulate movement of anions back and forth through fluorite crystal lattices. Phosphate (PO_4^{-3}) diffuses in this same manner between apatite crystallites that replace limestone. The cations of the original $CaCO_3$ do not move during the replacement process, i.e., the $CaCO_3$ does not go into solution and then precipitate the alteration product. The rate of diffusion does not change appreciably through 0 to 0.5 mm of CaF_2 or apatite crystallites, if experimental conditions remain constant, but one cannot calculate diffusion rates for these anions unless all of the system variables are known. These replacement reactions, calcite-apatite and calcite-fluorite, unlike the copper and iron chloride neutralization-precipitation limestone reactions reported by Garrels and Dreyer (1952), do not cease due to the layer of reaction product formed on the limestone. The reaction reported here proceeds until the limestone, up to a known diameter of one millimeter, is completely converted to fluorite.

Factors controlling $CaCO_3$ solubility are not the keys to limestone replacement processes, as postulated by Garrels and Dreyer (1952). In the presence of $NaHCO_3$-containing solutions, CaF_2 was altered to calcite, which was also extremely soluble in this same solution. The solubility of the replacement product in a given solution in relation to the solubility of calcite in the same solution is a better guide to replacement processes, although this is also a simplification. Certain replacement reactions that would result in highly insoluble products do not proceed at measurable rates at temperatures up to 75° C. The replacement of

$SrCO_3$ by $SrSeO_4$ is an example, or $MgCO_3$ by MgF_2. The activation energy for these replacement reactions is probably prohibitively high, resulting in extremely slow replacement rates.

Field occurrences indicate that the temperature of formation of non-uraniferous fluorite deposits is higher than that of uraniferous deposits (Gabelman, 1955). The reverse trend of U^{VI} removal with temperature accounts for this low-temperature, uraniferous-fluorite association, assuming that there is uranium present in the limestone-altering solution. The U^{VI} at higher temperatures may occur in a separate phase under the right conditions, or remain in solution.

The probable cause of this lessened U^{VI} removal with rising temperature is the requirement that four F^- ions in the neighborhood of the U^{VI} ion be replaced by four O^{-2} ions, or $(UO_4)^{-2}$ substitutes for the group $(CaF_4)^{-2}$. Oxygen must be available in the influent solution for this substitution to occur, and the amount of oxygen dissolved in the solution is inversely proportional to the solution temperature. For example, in Figure 3 there are approximately 0.0016g of oxygen dissolved in 100g of water at 75°C and one atmosphere. The U^{VI} C/C_o value associated with this temperature is 0.47. At 25°C 0.0039g of oxygen are dissolved in 100g of water and the associated C/C_o value should equal $\frac{0.0016}{0.0039} = \frac{x}{0.47}$, or 0.19. The C/C_o value obtained experimentally at 25°C was 0.185. It does not follow that natural fluorite replacement deposits developed under one atmosphere of pressure, but it does follow that temperature affects the quantity of dissolved oxygen that in turn affects U^{VI} substitutions.

Sr^{+2}, on the other hand, requires no lattice changes, and Ce^{+3} substitutions can be compensated electrostatically by omitting an occasional Ca^{+2} (2 Ce^{+3} for 3 Ca^{+2}). Reduction of the U^{VI} to U^{IV} is not required for substitution in fluorite any more than in apatite (Ames, in press). The substitution of U^{VI} in apatite during the calcite-phosphate reaction follows the normal trend of increasing U^{VI} removal with increasing temperature.

The inclusion of Ce^{+3} and Sr^{+2} within the fluorite lattice is rather similar as regards C/C_0 values, while U^{VI} shows considerably diminished C/C_0 values under comparable experimental conditions. The low C/C_0 values obtained for Ce^{+3} and Sr^{+2} indicate that these two cations can be present in all fluorites, regardless of temperature of formation.

Sellaite was not a stable phase in the kinetic system dolomite-NaF. Field occurrences also indicate the absence of sellaite in fluorspar replacement deposits of dolomite. The X-ray patterns of several samples from the Thomas Range, Utah deposits showed no sellaite. Magnesite is the stable phase in the magnesite-NaF system within the experimental conditions of this study. During dolomote replacement, the stable CaF_2 remains behind while the magnesium is removed. The result is a boxwork structure for the remaining fluorite.

It should be noted that surface area is directly proportional to the rate of reaction of calcite with alkaline, fluoride-bearing solutions. It follows, then, that higher permeability limestones should be replaced to a greater extent than lower permeability limestones in contact with the same replacing solution (Hove, 1947). Therefore, the "most favorable bed" becomes relative from district to district, as postulated by McKinstry (1955).

One cannot assume that present-day limestone permeability measurements will necessarily be of value in indicating which beds were favorable for replacement at the time of ore deposition. Further, it is unwise to emphasize the importance of this single variable in CaF_2 deposition. There are at least five more system variables that can be just as important and have little or nothing to do with the physical or chemical state of the limestone. One cannot flatly state that pH, temperature, CO_2 pressure, or some other simple variable is the most important in the replacement of $CaCO_3$ by CaF_2 when ore deposits could result from favorable conditions of any variable.

During both the calcite-apatite and calcite-fluorite replacement reactions, only the anions of the replaced solid move into the solutions. The cations are essentially "fixed" during this lattice rearrangement. Garrels and Dreyer (1952) reported a type of replacement reaction that involved movement of both anions and cations. Reactions involving movement of cations only, or movement of first the cations and then the anions, are now under study. The point is that the term "replacement" is exceedingly broad and includes many reaction types.

The importance of these replacement reactions to geological processes is easily discernible. By adding a few parts per million fluoride to an alkaline solution, and passing this solution over a calcite bed, a fluorite deposit is formed by replacement with a solution whose calcium and fluoride concentrations never exceed the Ksp for CaF_2 in that solution.

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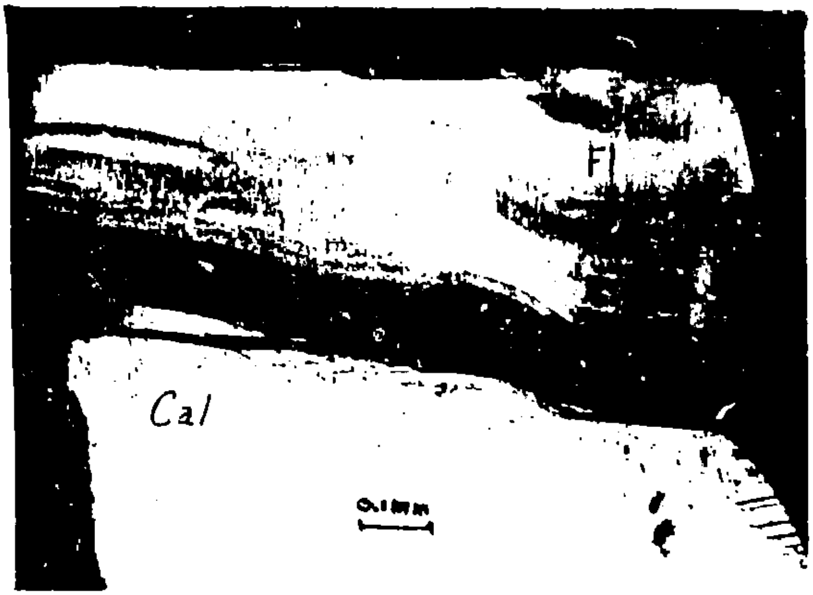

Plate 1. A calcite rhomb, sectioned parallel to $10\bar{1}1$, showing the fluorite replacement layer.

Cal = calcite. Fl = fluorite.

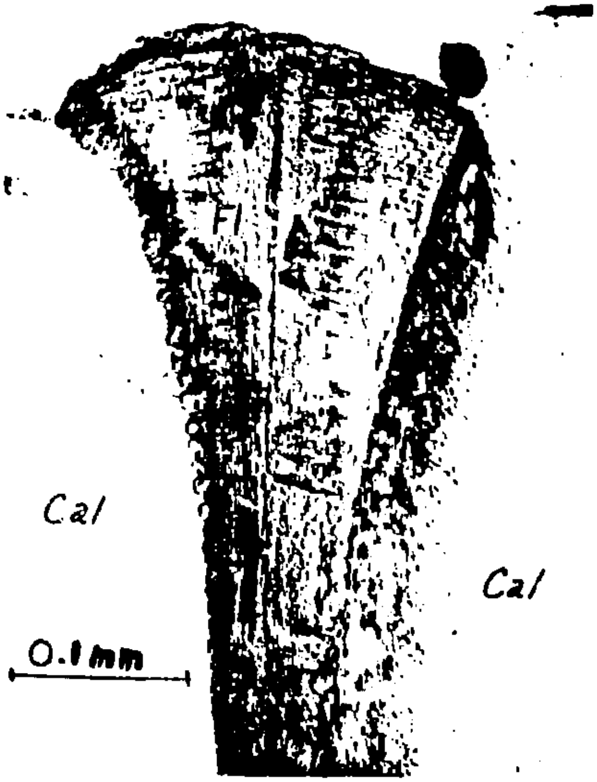

Plate 2. Fluorite replacement of calcite along a cleavage crack in the original calcite.

Cal = calcite. Fl = fluorite.

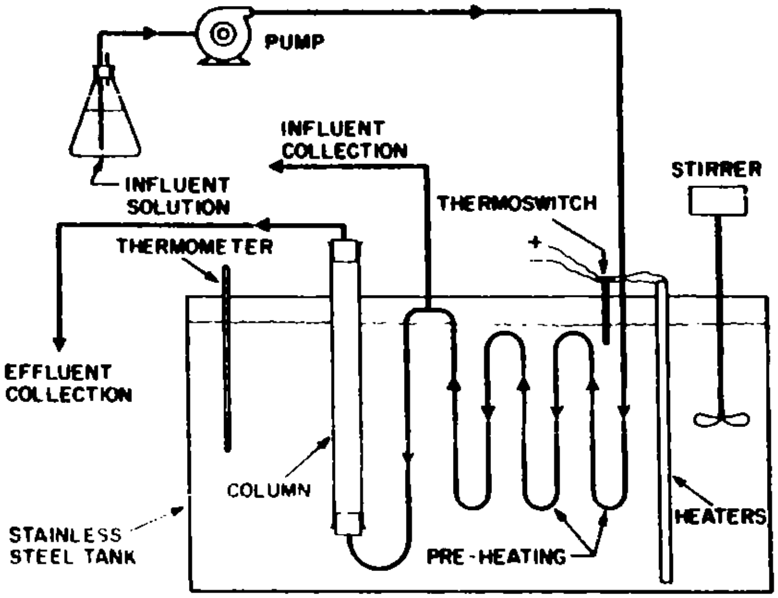

Figure 1. Experimental apparatus.

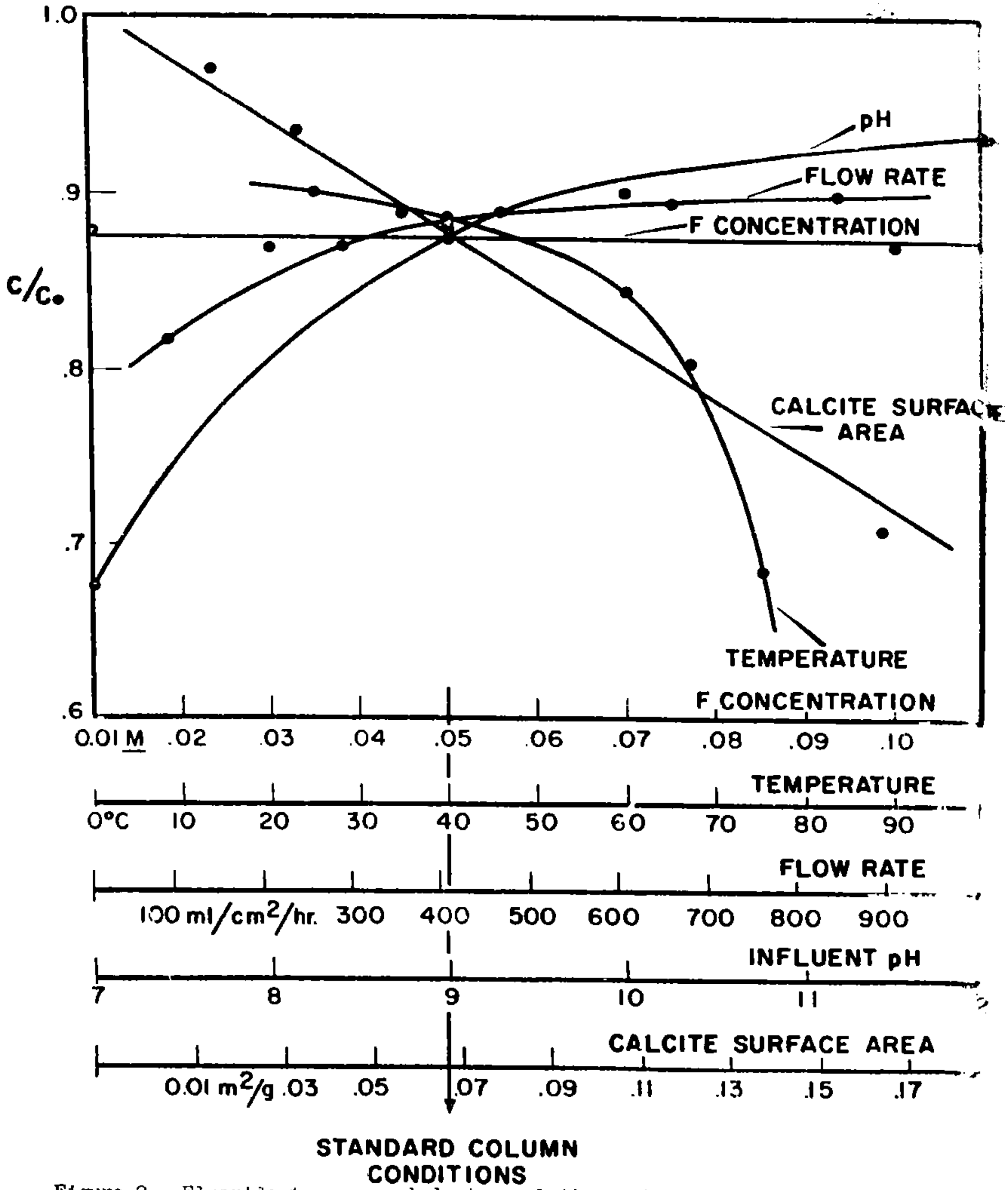

Figure 2. Fluoride ion removal during calcite replacement by alkaline, fluoride-bearing solutions. Fifty-gram calcite columns were used to obtain these data. All solutions contained 1M NaCl in addition to their other constituents.

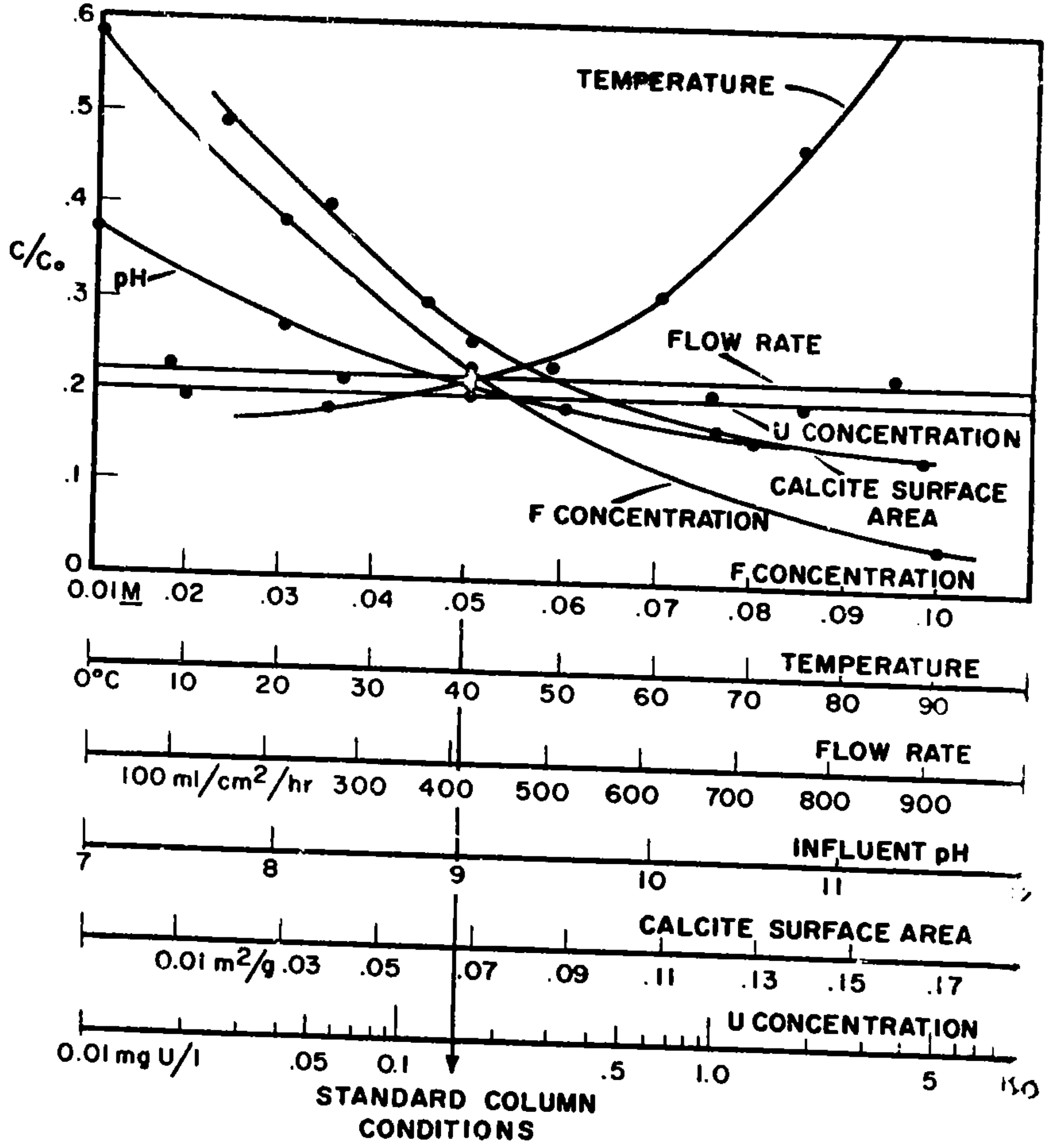

Figure 3. Uranyl ion removal during calcite replacement by alkaline, fluoride-bearing solutions. Fifty-gram calcite columns were used to obtain these data. All solutions contained 1M NaCl in addition to their other constituents.

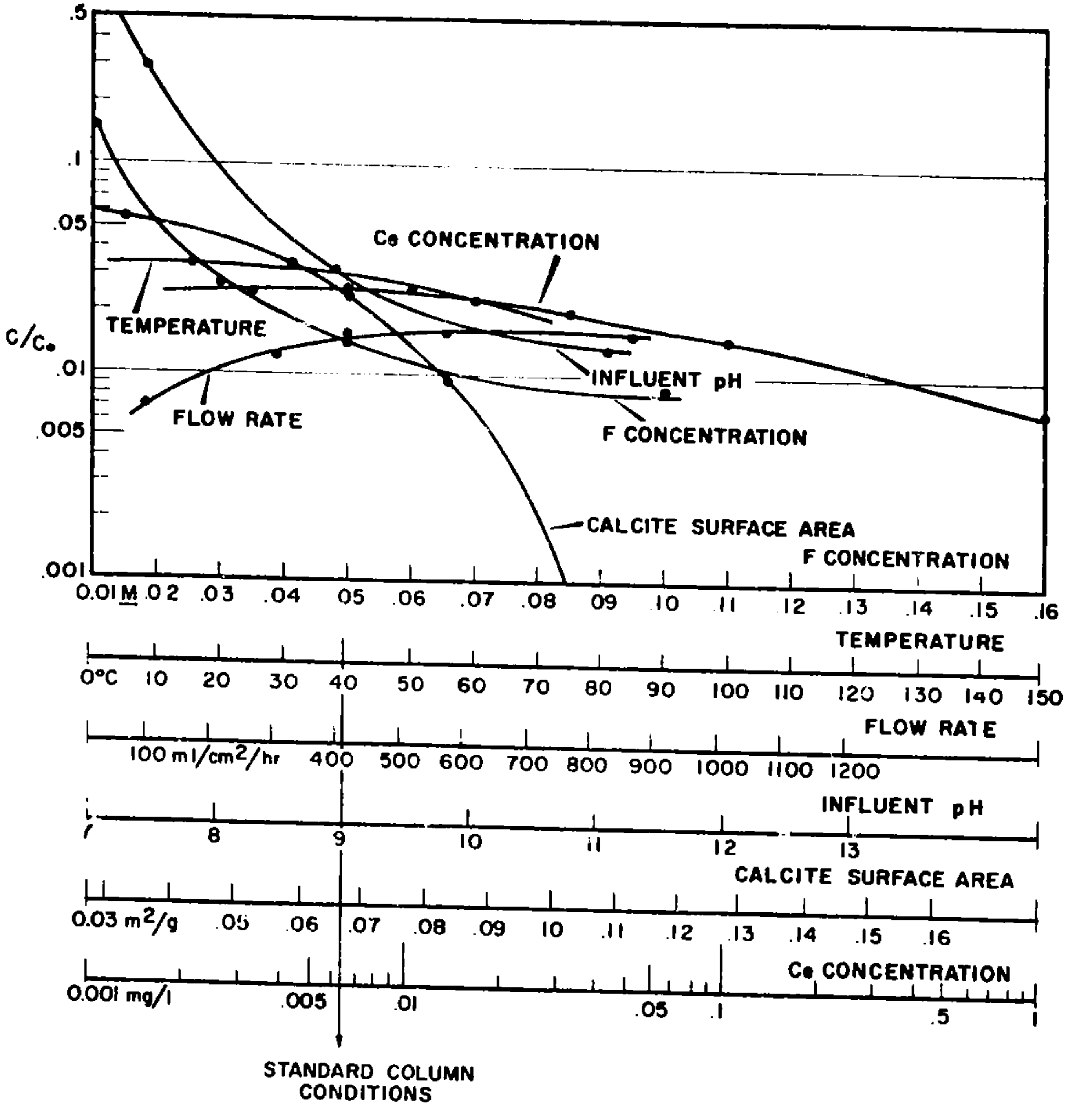

Figure 4. Ceric ion removal during calcite replacement by alkaline, fluoride-bearing solutions. Fifty-gram calcite columns were used to obtain these data. All solutions contained 1M NaCl in addition to their other constituents.

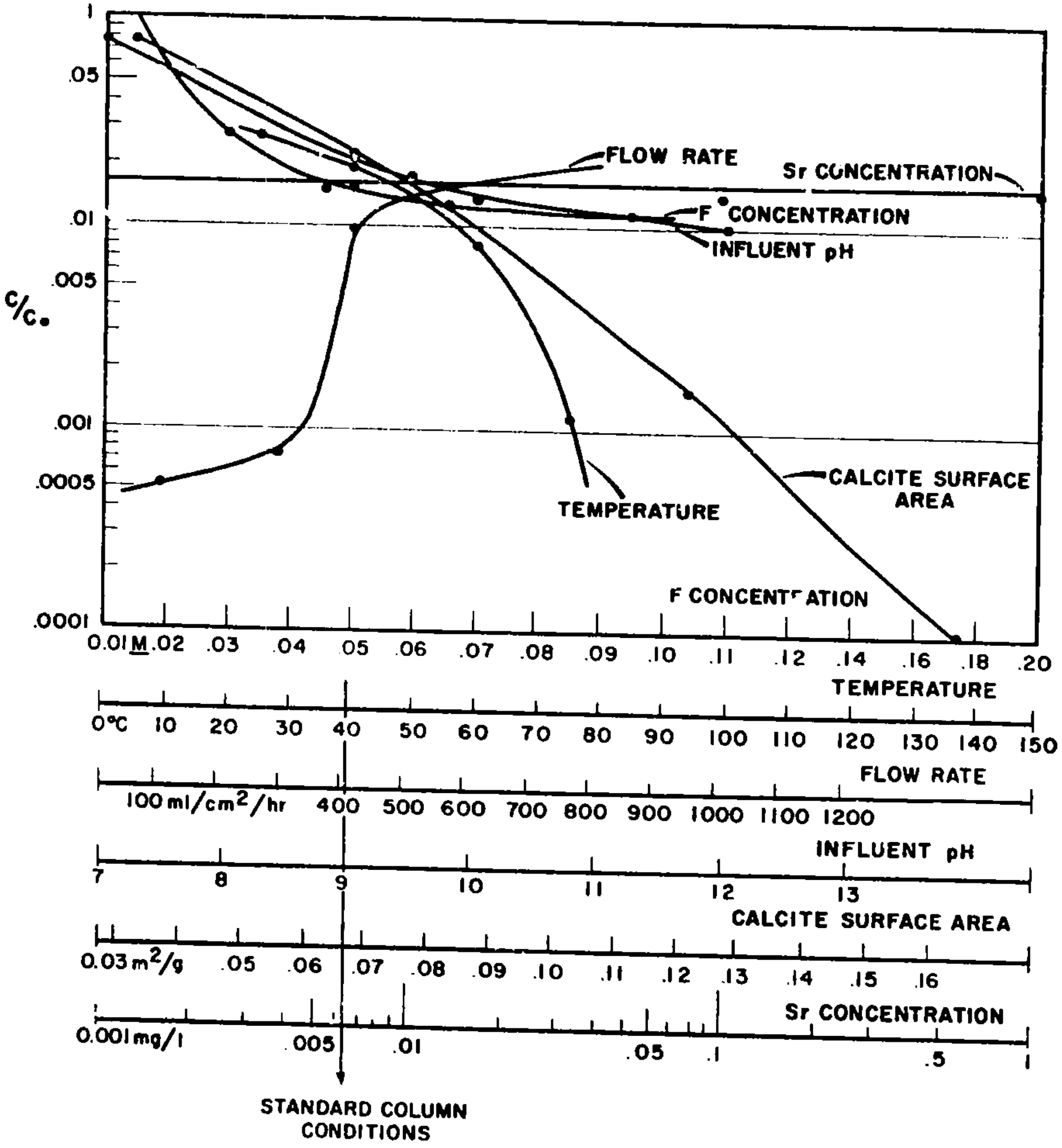

Figure 5. Strontium ion removal during calcite replacement by alkaline, fluoride-bearing solutions. Fifty-gram calcite columns were used to obtain these data. All solutions contained 1M NaCl in addition to their other constituents.