

# Strontium Sorption Studies on Crandallite

By IRVING MAY, MARIAN M. SCHNEPFE, and CHARLES R. NAESER

CONTRIBUTIONS TO GEOCHEMISTRY

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GEOLOGICAL SURVEY BULLETIN 1144-C

*Study of the interaction of  
crandallite with dilute cesium  
and strontium solutions.*

*Prepared on behalf of the  
U.S. Atomic Energy Commission*



**UNITED STATES DEPARTMENT OF THE INTERIOR**

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## CONTRIBUTIONS TO GEOCHEMISTRY

### STRONTIUM SORPTION STUDIES ON CRANDALLITE

By IRVING MAY, MARIAN M. SCHNEPFE, and CHARLES R. NAESER

#### ABSTRACT

Crandallite ores may be useful in the treatment of nuclear-waste solutions because of their reactivity with strontium in weakly acid solutions and in alkaline solutions containing aluminum.

The exchange capacity of the crandallite sample studied is not very high, being 6 to 10 milliequivalents of strontium and 2 milliequivalents of cesium per 100 grams of active phosphatic material. However, strontium removal is many times more effective in alkaline solutions, with precipitation being the dominant mechanism. The removal of strontium is even more complete in alkaline solutions containing aluminate ions.

#### INTRODUCTION

The interaction of crandallite with strontium solutions was studied in the laboratory in order to evaluate the possible use of crandallite as a scavenging agent for strontium-90 in waste solutions resulting from the reprocessing of reactor-fuel elements.

Ames (1960) has studied the removal of strontium from solution by a replacement reaction in which apatite is formed in the interaction of alkaline phosphate solutions with calcite. Thomas and others (1960) have reported studies of the sorption of strontium by vermiculite, variscite  $[\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4]$ , Tennessee rock phosphate, and Florida pebble phosphate.

Crandallite is a hydrated basic phosphate of calcium and aluminum. Its formula,  $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ , corresponds to that of minerals having the alunite-type structure,  $\text{A}^{+1}\text{B}_3^{+3}(\text{SO}_4)_2(\text{OH})_6$ . The enrichment of strontium in minerals having the alunite structure, and more particularly in crandallite, has been reported by Frondel (1958a,b). Where it is not an essential constituent, as in goyazite, as much as 3 percent SrO may be found.

Large deposits of crandallite have been described by Altschuler, Jaffe, and Cuttitta (1956) in a zone of aluminum phosphate overlying the commercially mined apatite deposits of the Pliocene Bone Valley Formation in west-central Florida. This zone contains quartz, millisite  $[(\text{Na,K})\text{CaAl}_6(\text{PO}_4)_4(\text{OH})_9 \cdot 3\text{H}_2\text{O}]$ , and wavellite  $[\text{Al}_3(\text{OH})_3 \cdot$

$(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}]$  in addition to crandallite. As the crandallite is derived from supergene alteration of the apatite deposit, its composition varies with depth.

The rock of the aluminum phosphate zone is friable, porous, and highly leached. It is thus readily amenable to beneficiation because the reactive phosphatic fraction can be crushed easily and separated from the coarser quartz.

These deposits are of economic interest because the aluminum phosphate zone extends over several hundred square miles and has an average thickness of 6 to 7 feet. The known reserves of these deposits, of which crandallite is a major mineral, exceed 800 million tons (Altschuler, Jaffe, and Cuttitta, 1956). Several million tons of rock from the aluminum phosphate zone are stripped annually in mining the calcium phosphate deposits.

Crandallite is of especial interest as a scavenging agent for strontium because it is more resistant to solution by dilute mineral acids than most phosphate minerals and, unlike apatite, it is insoluble in both alkaline and carbonated ground waters.

Crandallite deposits thus provide a stable, cheap, and commercially available material for possible use in the removal of strontium from nuclear-waste solutions.

The work was undertaken by the Geological Survey on behalf of the Division of Reactor Development, U.S. Atomic Energy Commission, as a part of a study of nuclear-waste disposal.

#### MATERIAL USED

The material studied was a sample of crandallite ore from the Pliocene Bone Valley Formation of Homeland, Fla. The sample had been studied previously (oral communication, Z. S. Altschuler, U.S. Geological Survey) and was known to contain major quartz and crandallite, subordinate millisite, and minor (1–5 percent) quantities of apatite, goethite, and kaolinite. This sample is closely related in petrographic character and mineral composition to material from the middle strata of the leached zone studied by Altschuler, Jaffe, and Cuttitta (1956, p. 501). A spectrographic check by Helen Worthing, U.S. Geological Survey, showed the presence of 0.07 percent strontium and less than 0.003 percent cesium. The chemical analysis of this sample is given in table 1.

Quartz was isolated and determined to make up 41 percent of the sample by using Talvitie's (1951) procedure, in which the sample is heated for 20 minutes with phosphoric acid at 250°C to dissolve minerals other than quartz. A microscopic examination of the isolate showed that it was almost pure quartz, with an occasional grain of zircon. The amount of quartz agrees reasonably well with the total

TABLE 1.—*Chemical analysis of crandallite ore*

[Analysis by chemists of the U.S. Geol. Survey using the methods of Shapiro and Brannock (1956)]

	<i>Percent</i>		<i>Percent</i>
SiO <sub>2</sub> -----	46.9	K <sub>2</sub> O-----	0.18
Al <sub>2</sub> O <sub>3</sub> -----	18.3	H <sub>2</sub> O-----	9.7
Fe <sub>2</sub> O <sub>3</sub> -----	2.0	TiO <sub>2</sub> -----	.65
FeO-----	.06	P <sub>2</sub> O <sub>5</sub> -----	15.8
MgO-----	<.10	MnO-----	.03
CaO-----	5.9	CO <sub>2</sub> -----	.3
Na <sub>2</sub> O-----	.56		
		Total-----	100.5

silica content of 46 percent. The fact that phosphoric acid attacks quartz slightly, may cause the SiO<sub>2</sub> to deviate from accuracy by 2± percent for a sample of this particle size.

Calculations based on the chemical analysis of the sample and on the theoretical formulas of the minerals give the following mineralogical composition:

	<i>Percent</i>
Quartz-----	41
Crandallite-----	34
Millisite-----	15
Apatite-----	2
Others-----	8
Total-----	100

## STUDIES OF STRONTIUM SORPTION

### COLUMN EXPERIMENTS

All column studies were made with 12-mm-diameter glass columns (fig. 1), the lower parts of which were immersed in a constant-temperature water bath. Flow rates were regulated by manipulating the stopcock or by applying nitrogen pressure to the head of the column. Asbestos mats served as column supports.

A preliminary sorption experiment was made with a 12-mm-diameter column containing 40 g (grams) of a +35-mesh fraction of sample gently crushed to pass 20 mesh. A strontium solution containing 100 µg Sr per ml (micrograms of strontium per milliliter) with a few drops of free nitric acid and spiked with approximately 0.08 µc per ml (microcurie per milliliter) of strontium-89 was passed through the sample at room temperature by gravity flow averaging 10 ml per hr (milliliter per hour). The eluate was collected in 10-ml fractions. The pH of the eluate was 6.6, which is close to the equilibrium pH of 6.3 for the sample.

The concentration of strontium in each of the fractions was determined with a Geiger-Müller counter by counting the beta activity of 1-ml aliquots evaporated in aluminum planchets. The feed solution

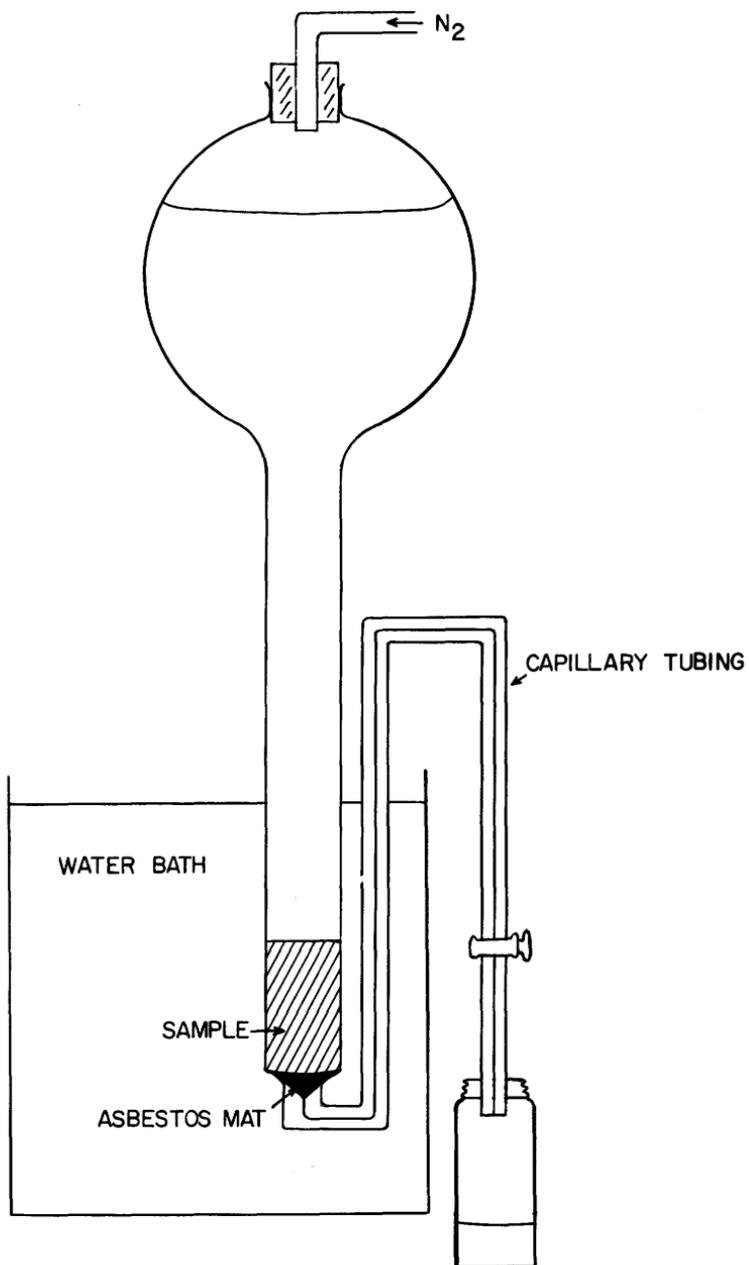


FIGURE 1.—Sorption apparatus.

gave counts approximately 500 times the background level of 20 counts per minute. The experiment was discontinued after 380 ml of eluate was collected.

A well-defined breakthrough curve (fig. 2) was obtained, with a breakthrough capacity (strontium uptake before the first detectable strontium in the eluate) of 1.54 meq (milliequivalents) Sr per 100 g.<sup>1</sup> For a symmetrical breakthrough curve under these conditions, a total capacity of 1.8 meq Sr per 100 g is indicated from the point where the ratio of the concentration of strontium in the eluate to the initial concentration ( $C/C_0$ ) equals 0.5 (Samuelson, 1953). At the conclusion of the experiment, a  $C/C_0$  value of only 0.8 was attained, with indications of some leveling of the curve; the total strontium uptake was 1.9 meq Sr per 100 g.

Determinations of  $P_2O_5$  made on representative fractions of eluate gave a  $P_2O_5$  range of from 50 to 100 ppm (parts per million), and this indicated the solubility of phosphatic material under these conditions, or the hydrolytic evolution of phosphate.

In view of the well-known incongruous solubility of the basic calcium phosphates, the conditions of this experiment would probably favor the formation of an apatitelike phase,  $A_{10}(XO_4)_6(OH)_2$ , rather than a less basic compound. This follows from the hydrolysis behavior of calcium phosphates in which compounds more acid than apatite, including tricalcium phosphate,  $A_3(XO_4)_6$ , tend to hydrolyze to the stable apatite form with liberation of excess phosphoric acid.

Subsequent experiments were performed with a representative split of the sample that was gently crushed. The particle-size distribution of the crushed material was as follows: less than 1 percent was coarser than 20 mesh; 16 percent was in the -20 to +35 range; 61 percent was in the -35 to +100 range; and 23 percent was finer than 100 mesh.

The sample was sufficiently fine to enable the use of 12-mm-diameter columns without channeling problems. However, to facilitate a good rate of flow, the sample was usually blended with twice its weight of 80- to 100-mesh acid-washed silica sand. Feed solutions contained 50 ppm Sr and were spiked with strontium-89.

A check of the strontium sorption by 4 g of the silica sand and 18 mg (milligrams) of asbestos indicated that the uptake of the blank was insignificant.

The effect of pH on the strontium uptake was studied in column experiments using buffered and unbuffered solutions containing 1 or 2 grams of crandallite (table 2). The solution was buffered at pH 3 by adding 0.05 moles of sodium acetate and hydrochloric acid per liter (fig. 3). The solutions buffered at approximately pH 6 were

<sup>1</sup> Unless otherwise indicated, all capacities are calculated on the basis of the crandallite sample including natural associated quartz.

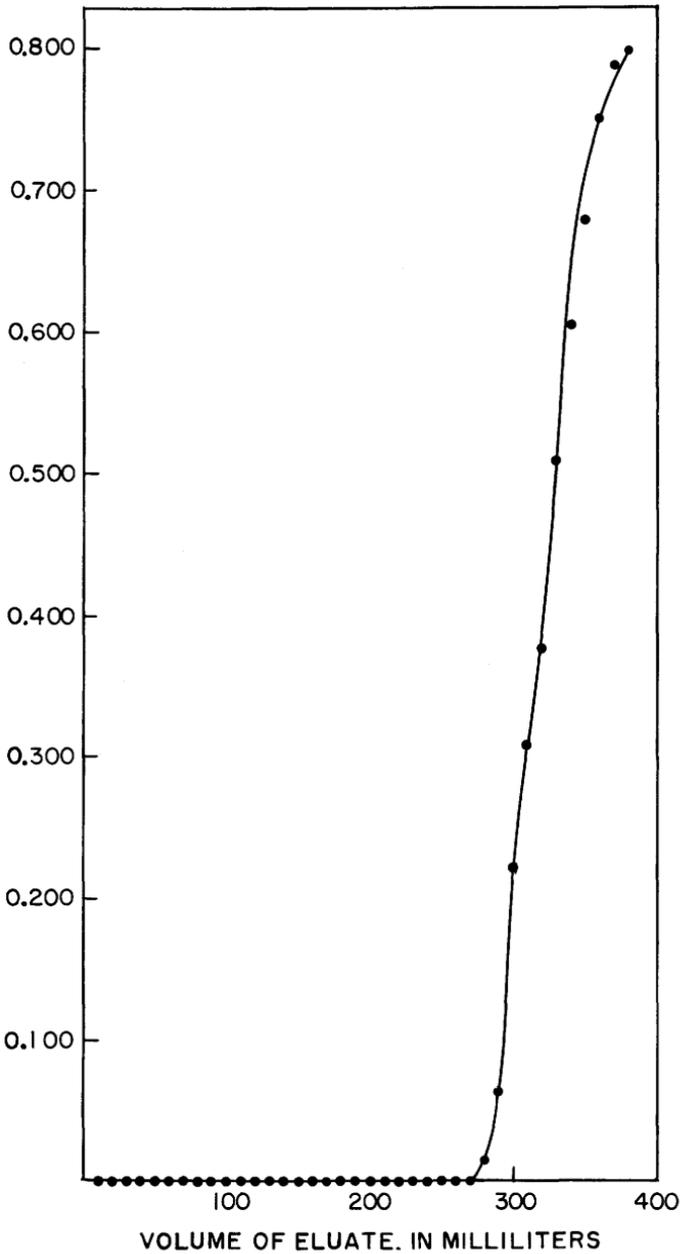


FIGURE 2.—Sorption of strontium by 40 g of crandallite ore (+35-mesh fraction).  $C_0=100$  ppm Sr.

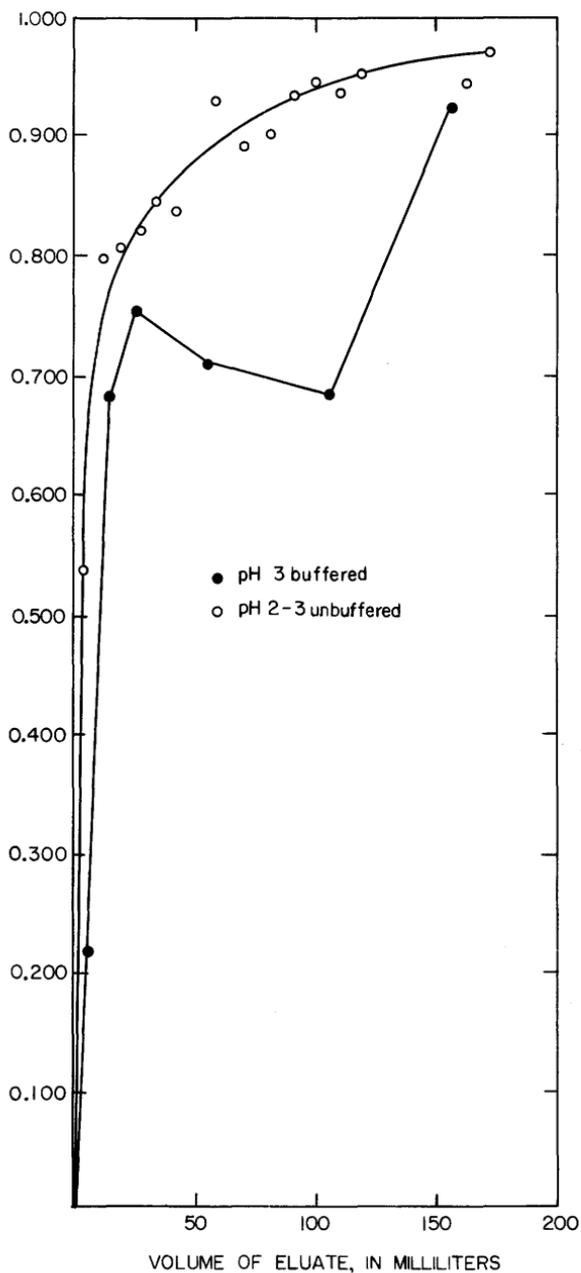


FIGURE 3.—Strontium removal from solutions at pH 3 by crandallite.  $C_0=50$  ppm Sr.

TABLE 2.—Summary of column experiments, pH range 2 to 10

Crandallite sample weight (g)	Contacting solution		Average flow rate (ml per min per square cm)	Total uptake (meq per 100 g)		See figure—	
	Total volume of eluate (ml)	pH		Experimental <sup>1</sup>	Calculated <sup>2</sup>		
		Buffered					Unbuffered
<b>Strontium, 50 ppm</b>							
2.....	222		2-3		3 0.94	0.3	3
2.....	180	3			2 2.7	.6	3
1.....	200	5.7		0.5	6 6.3	4.1	4
2.....	200	5.7		.4	5 5.8	4.7	4
1.....	290	6.0			5 5.5	2.6	4, 6
1.....	380		6.0	.4	5 5.5	2.6	4
1.....	290	6.0		.6	7 5.7	3.3	6
1.....	270	5.5		.6	7 6.6	5.0	6
1.....	470		10.5	.7	27 7.0	11.4	5
<b>Cesium, 50 ppm</b>							
1.....	80	6.0		0.07	1 1.4	1.3	9
1.....	210		6.0	.7	1 1.6	1.1	9

<sup>1</sup> Experimental uptake. Total decrease in strontium content of the feed solution after passing through the column.

<sup>2</sup> Calculated uptake. Value obtained from the abscissa corresponding to the point  $C/C_0=0.5$ .

<sup>3</sup> Room temperature.

<sup>4</sup> Buffer. Sodium acetate and hydrochloric acid (0.05 moles of each per liter).

<sup>5</sup> Buffer. Sodium dihydrogen phosphate (0.005M+NaOH).

<sup>6</sup> Experiment made at 30°C with the aid of a thermostatically controlled water bath.

<sup>7</sup> Experiment made at 55°C with the aid of a thermostatically controlled water bath.

0.005M with respect to sodium dihydrogen phosphate; the pH was adjusted with dilute sodium hydroxide solution. Inasmuch as phosphate was dissolved in small amounts from the sample by mildly acidic or alkaline solutions, the presence of added phosphate did not represent a drastic change in the system.

Flow rates of approximately 10 ml per 15 minutes (0.6 ml per min per sq cm) were maintained, when possible, by partly closing the stopcock or by applying external pressure. In most of the experiments made with solutions ranging from pH 5 to pH 8, slow flow rates required the application of as much as 7 psi (pounds per square inch) of nitrogen to maintain the desired flow. Even with the application of pressure, however, some flow rates were much less than 10 ml per hr; experiments with very slow flow rates were discontinued after approximately 1 day.

At pH 6, the strontium uptake is the same, within the experimental error, for the buffered and unbuffered solutions (fig. 4; table 2). As anticipated, the unbuffered solutions, especially those with pH values differing considerably from the equilibrium pH of the crandallite, underwent a large change in pH; this was most pronounced in the first eluate fractions.

Marked trends are apparent in the total strontium uptake as a function of pH, although it is recognized that strict comparisons may not be justifiable because of variations in volumes of feed solution

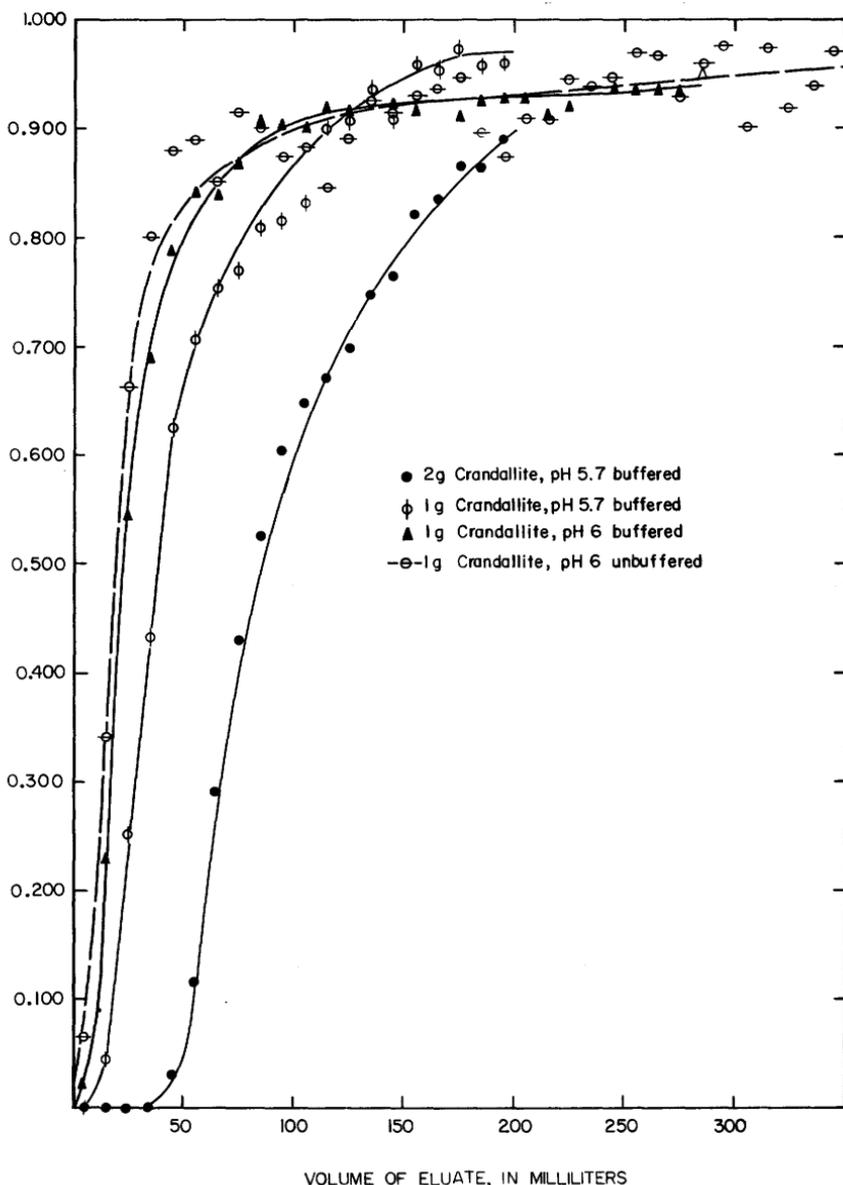


FIGURE 4.—Strontium removal from weakly acid solution by crandallite.  $C_0 = 50$  ppm Sr.

and in contact time. The total observed strontium uptake from unbuffered solutions at pH 3, 6, and 10.5 were 1, 6, and 27 meq Sr per 100 g, respectively. It is of interest to compare these values with the total exchange-capacity values of 0.3, 1.5 and 8.5 meq Sr per 100 g derived from the 50-percent breakthrough capacities. The relatively large difference between corresponding capacities suggests a precipita-

tion reaction occurring simultaneously with the sorption. At high pH values the precipitation reaction predominates, a precipitate forming as a discrete layer on the column bed.

It may be concluded from the column-experiment data that the differences in the experimental and calculated uptake represent the amount of precipitation. It is apparent that this difference increases with pH.

In the region of pH 3 there is relatively little removal of strontium from buffered or unbuffered solutions. As shown in figure 3, even the first 10 ml of eluate contain strontium, and the  $C/C_0$  values thereafter rise sharply.

In the pH range of 5 to 6, the strontium uptake from feed solutions was greater than at pH 3. With increasing pH there is not only an increase in breakthrough capacities but a more gradual rise in the  $C/C_0$  values, and the curve tends to flatten at values lower than 1.0. The phosphate buffer does not alter significantly the strontium-uptake capacity of the system.

At pH 10.5, strontium uptake is greater than at lower pH values (fig. 5); the  $C/C_0$  value never exceeds 0.7. The strontium capacity of the column charge was partly regenerated after standing overnight.

Experiments were made at 30° and 55°C with 1 g portions of crandallite and a solution at pH 6 to determine the temperature effect on the strontium uptake (fig. 6). The strontium sorption did not differ significantly for these two temperatures, being 5.5 and 5.7 meq Sr per 100 g, respectively.

Experiments were also made with solutions having the approximate alkali content of tank supernatant liquid of a typical alkali-treated Savannah River waste solution. The solution used was 0.46M with respect to sodium hydroxide and had 18.3 ppm Sr. In a column experiment with a 1-g charge of crandallite, all the strontium was removed from the first 30 ml of feed solution; that is, the breakthrough capacity equaled 550  $\mu$ g Sr (fig. 7.). The  $C/C_0$  value then rose as high as 0.6–0.7 at the end of the day's run of 280 ml of solution. After a night's interruption, the next 60 ml of eluate had  $C/C_0$  values no higher than 0.007, but these values then rose slowly during the day to a maximum of 0.45. Again the  $C/C_0$  value dropped off overnight to 0.004 (total volume of the eluate at this point was 560 ml). The  $P_2O_5$  content of the eluate fractions was inversely related to the strontium content. The  $P_2O_5$  value of the fractions collected at the start of the run and after each night's interruption exceeded 200 ppm. In other fractions, the  $P_2O_5$  content ranged from 15 to 120 ppm.

A precipitate was clearly discernible on the upper surface of the column bed. Although it was not possible to isolate it completely from the crandallite packing, some identification tests were attempted,

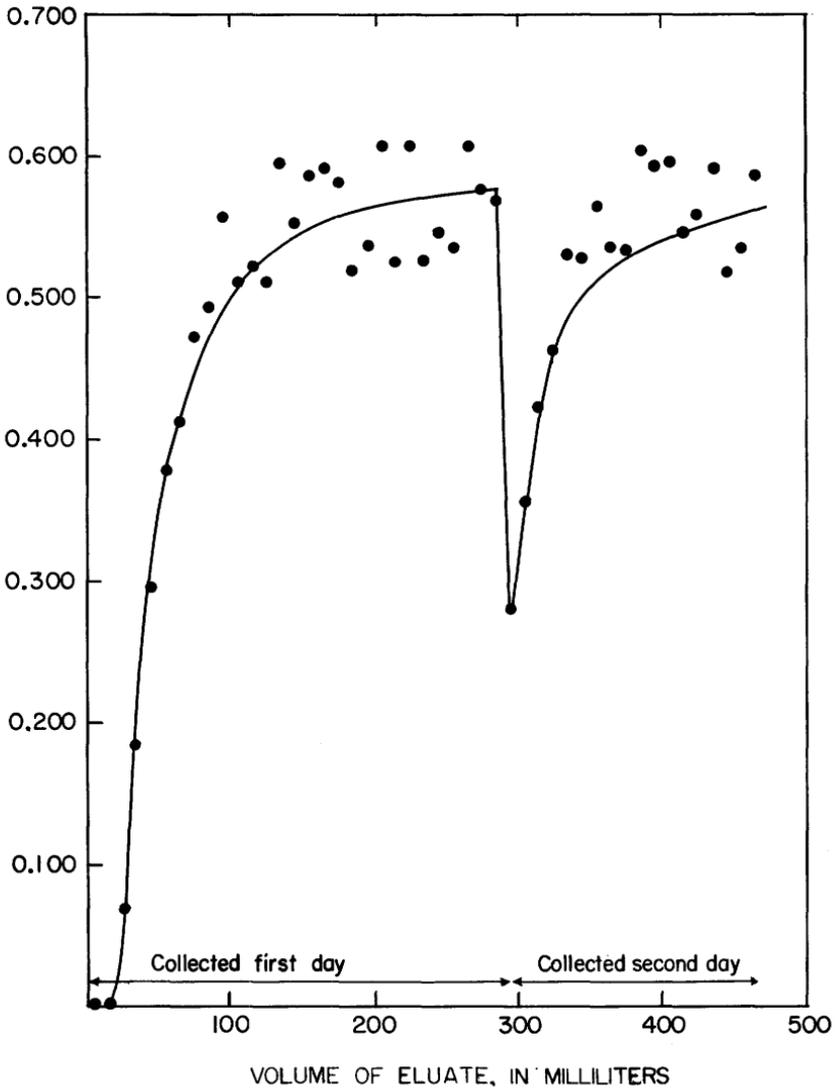


FIGURE 5.—Strontium removal from solution at pH 10.5 by crandallite.  $C_0 = 50$  ppm Sr.

but the results were not wholly conclusive. Infrared tests by Irving Breger, U.S. Geological Survey, could not establish the presence of either strontium carbonate or strontium orthophosphate. X-ray examination by Marie Lindberg, U.S. Geological Survey, showed the presence of apatite and quartz and a strong 2.90–2.91 Å reflection from Cu-K $\alpha$  radiation (possibly crandallite reflection); broad reflections were obtained indicative of poor crystallinity. It is likely that the strontium was present in the material having the structure of apatite. This is consistent with the findings of Denk and Boppel

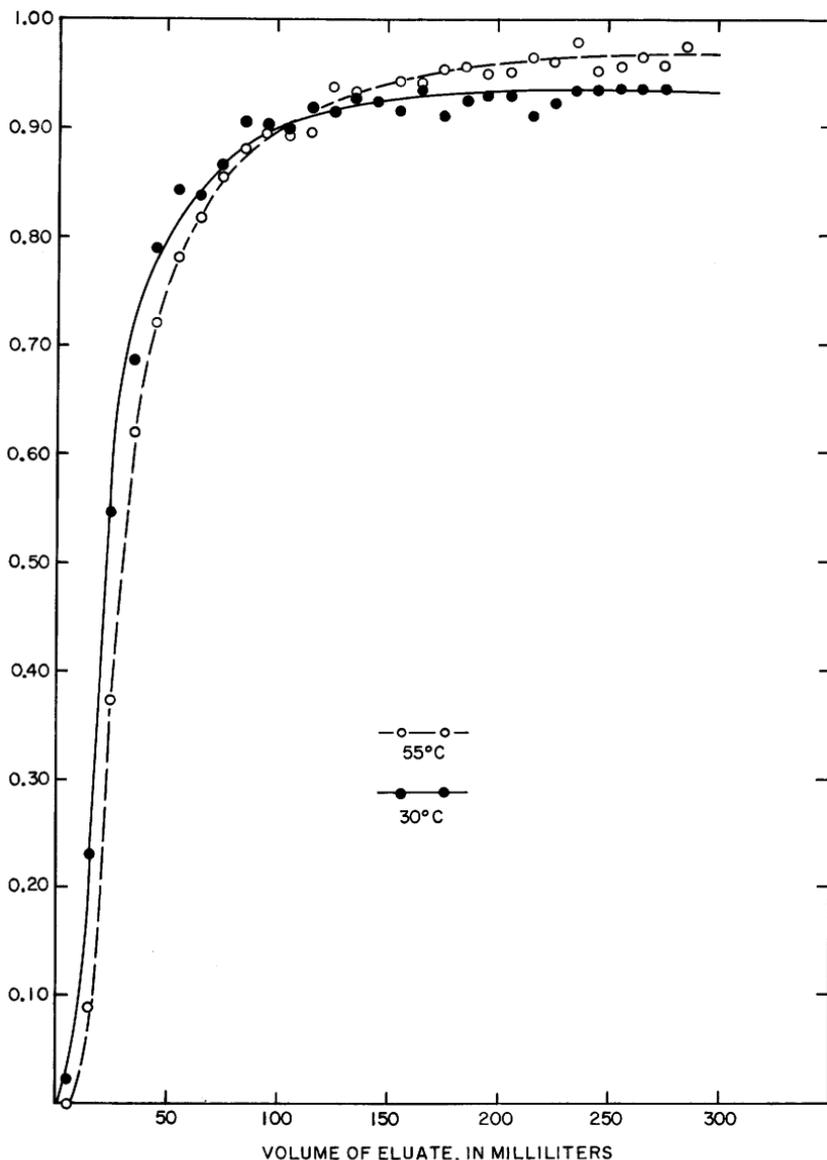


FIGURE 6.—Temperature effect on strontium removal by crandallite from solutions buffered at pH 6 (phosphate buffer).  $C_0=50$  ppm Sr.

(1961), who have recently reported the formation of apatite phases in the precipitation of strontium phosphate under similar conditions.

Aluminum is frequently present in nuclear wastes. Therefore, a column experiment was made to determine the effect of aluminum on crandallite's removal of strontium from a solution 0.5M with respect to sodium hydroxide (fig. 8). A 50-ppm strontium solution spiked

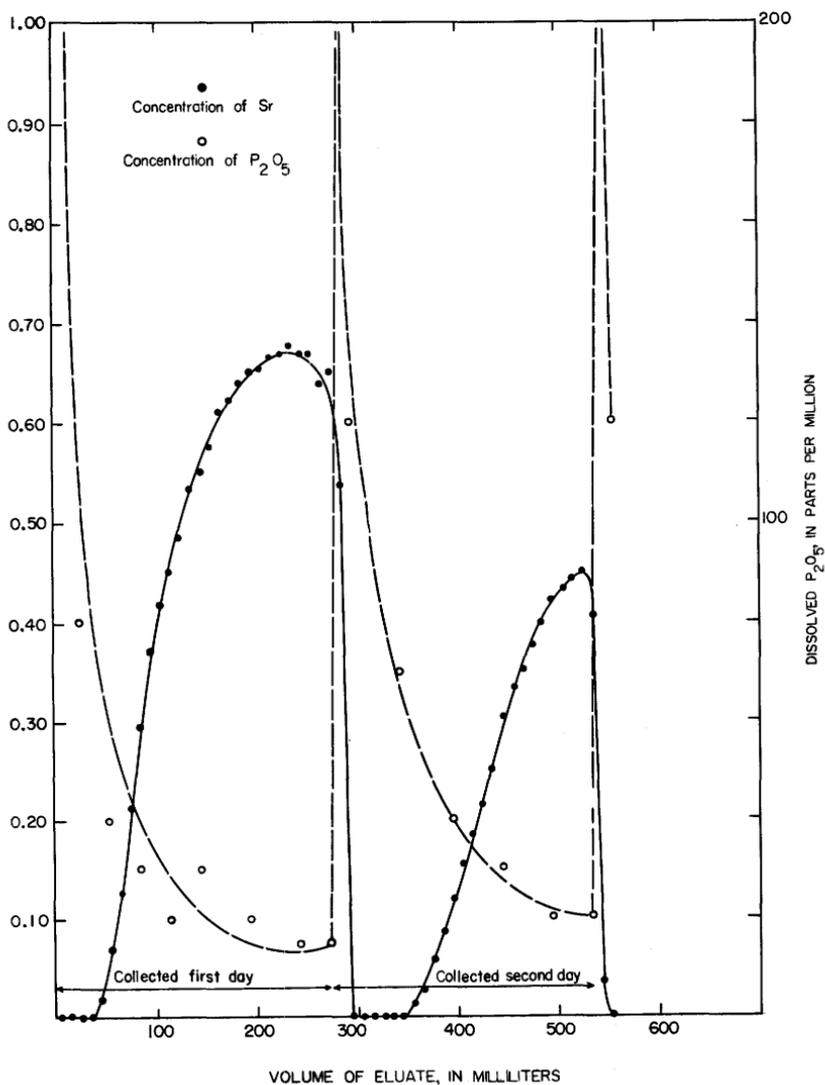


FIGURE 7.—Strontium removal from, and phosphate solution in, 0.46M NaOH with crandallite.  $C_0=18.3$  ppm Sr.

with strontium-89 was prepared containing 0.33 mg Al per ml in the form of sodium aluminate. Flow rates averaging 0.3 ml per min per sq cm were maintained; only at the latter part of the experiment was it necessary to apply 0.5 psi pressure to maintain this flow rate. A precipitate formed at the top of the column bed. A concentration of the radioactivity in the precipitate was readily determined with a portable monitor. The  $C/C_0$  values rose gradually after the first 30 ml of eluate, reached a maximum of 0.2 after the passage of 130 ml

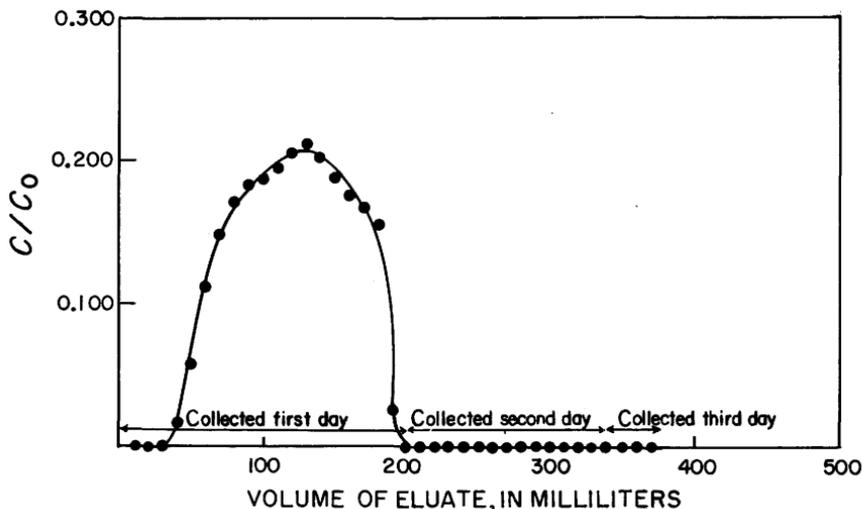


FIGURE 8.—Strontium removal by crandallite in the presence of aluminum.  $C_0=50$  ppm Sr.

of eluate, and then decreased with additional feed solution as the day's run progressed. The  $C/C_0$  values of the eluate for the next 2 days (170 ml) remained less than 0.002. A total of 370 ml of eluate were collected, from which 14.3 mg of strontium, or 32.5 meq Sr per 100 grams, were removed. Again, as with experiments at this alkalinity in the absence of aluminum, precipitation of strontium seems to be the predominant reaction.

#### BATCH EXPERIMENTS

Batch experiments were also made with strontium. Half-gram samples of crandallite were treated for 19 hours at room temperature with 10, 25, and 100 ml of 50-ppm strontium solution at pH 8.3. The percentages of strontium removed were 89, 65, and 31, respectively. Strontium concentration in the residual solutions ranged from 5 to 35 ppm even though there was a tenfold increase in the strontium in contact with a fixed sample weight.

A test of the concentration effect of strontium was made by treating quarter-gram portions of crandallite ore for 48 hours at room temperature with 50-ml volumes of 0.5M sodium hydroxide solutions containing varying concentrations of strontium. Strontium concentrations ranging from 2 to 50 ppm were reduced to 0.01–0.03 ppm.

Another batch experiment was made to determine the rate of the strontium removal from solution by the crandallite ore. Ninety-nine percent of the strontium was removed within 1 hour, and 99.9 percent was removed in 16 hours (table 3). The total strontium uptake corresponds approximately to that calculated from a column experiment with strontium solution at pH 10.5 (table 2).

TABLE 3.—Rate of strontium removal by 0.250 g of crandallite from 25 ml of 50-ppm Sr in 0.5M NaOH

Contact time (hr)	Residual Sr (ppm)	Total uptake (meq Sr per 100 g)
1	0.58	11.2
2	.30	11.3
4	.20	11.3
16	.02	11.4
256	.07	11.3

## SORPTION OF CESIUM

As cesium is a constituent of radioactive wastes, it was desirable to determine the extent to which crandallite would remove cesium from solution. Column experiments were made with 1-gram crandallite charges using 50-ppm cesium solutions spiked with cesium-137 (0.02  $\mu\text{c}$  per ml), both buffered and unbuffered, at pH 6. The count of the feed solution was approximately 700 times the background level. The activity of the eluate was measured with a sodium iodide-crystal scintillation counter. The unbuffered solution gave flow rates averaging 0.7 ml per min per sq cm without the application of external pressure. However, the buffered solution required 5 psi pressure even to maintain the slow flow rate of 0.07 ml per min per sq cm. The cesium appeared in the first 10 ml of eluate collected in each experiment, and the  $C/C_0$  values climbed rapidly thereafter (fig. 9). The pH of the unbuffered eluate ranged from 6.2 to 6.9, and that of the buffered eluate ranged from 5.5 to 6.1. The total volumes of eluate collected from the unbuffered and buffered solutions were 210 and 80 ml, respectively, giving exchange capacities of 1.6 and 1.4 meq Cs per 100 g.

A column experiment with cesium was also made using a 50-ppm cesium solution in 0.5M sodium hydroxide and 1 g of crandallite. The flow rate averaged 0.3 ml per min per sq cm without the application of pressure. The first 10-ml eluate fraction had a  $C/C_0$  value of 0.6; the  $C/C_0$  values then rose steeply to 1.0. The total exchange capacity equaled 0.2 meq Cs per 100 ml. The results indicate that the sodium ions offer serious competition to the exchange reaction of cesium with crandallite.

In a batch experiment, quarter-gram portions of crandallite were treated with various volumes of 50-ppm cesium solution buffered at pH 6. The solution volumes were 10, 25, 50, and 100 ml. After approximately 24 hours of contact time at room temperature, the supernatant liquids were removed and their cesium content determined (table 4). The pH of the supernatant liquid did not change. The data suggest the probability of an exchange rather than a precipitation mechanism. It can be seen that crandallite has a low exchange capacity for cesium.

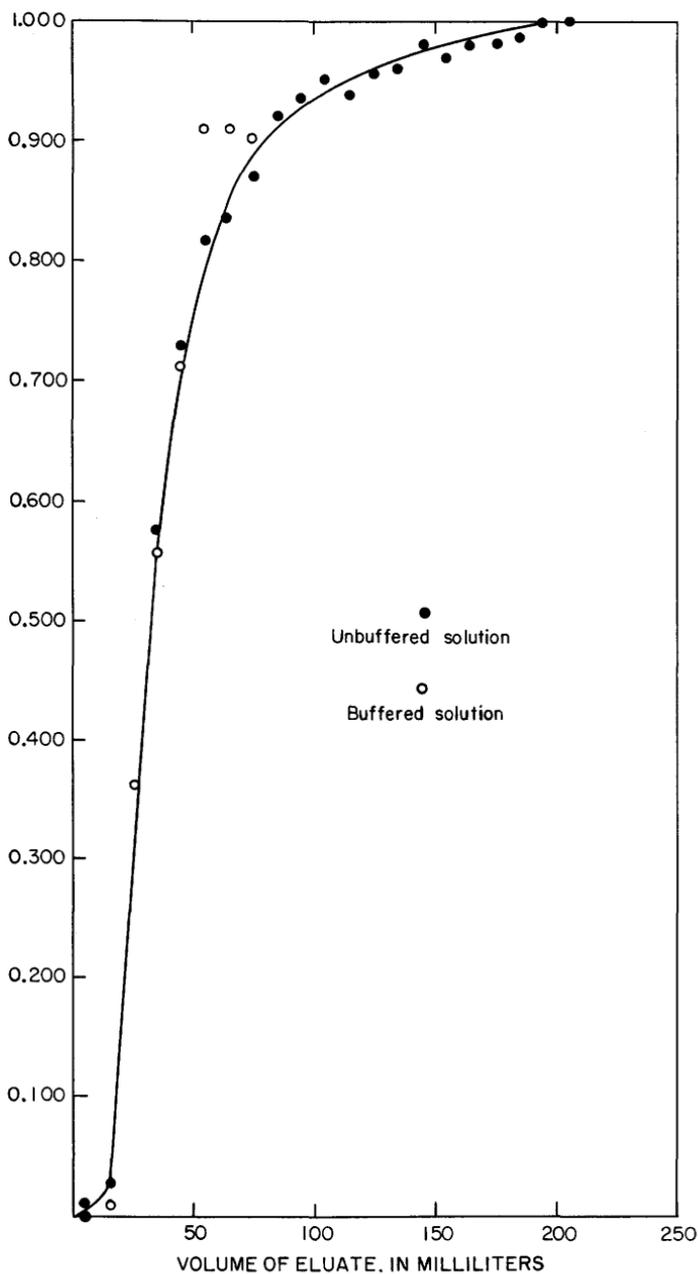


FIGURE 9.—Cesium removal from solutions at pH 6 by crandallite.  $C_0=50$  ppm Cs.

TABLE 4.—Cesium sorption by 0.250 g crandallite from various volumes of 50-ppm cesium solution buffered at pH 6

Solution volume (ml)	Residual Cs (ppm)	Total uptake (meq Cs per 100 g)
10	22	0.83
25	35	1.1
50	41	1.3
100	45	1.5

### SUMMARY

Breakthrough curves obtained in column experiments with crandallite and mildly acid strontium solutions indicate the occurrence of an ion exchange reaction. Strontium removal is many times more effective from alkaline solutions, with precipitation being the dominant mechanism. The removal of strontium is even more complete in alkaline solutions containing aluminate ions.

As expected, crandallite is much less effective in the removal of cesium, primarily owing to the absence of a precipitation reaction. The exchange capacity of the crandallite sample studied is not very high, being 6–10 meq Sr and 2 meq Cs per 100 g of active phosphatic material.

Crandallite ores may be useful in the treatment of nuclear-waste solutions because of their reactivity with strontium in weakly acid solutions and in alkaline solutions containing aluminum.

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