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Separation of Strontium and Barium from Calcium Compounds

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Abstract

Results are presented of an investigation with radioactive isotopes ^{85}Sr and ^{133}Ba of processes of strontium and barium coprecipitation with calcium hydroxide and calcium oxalate for the preparation of calcium carbonate with a very low content (less than 1 ppm) of strontium and barium.

INTRODUCTION

Strontium and barium (besides magnesium) are the main impurities of numerous calcium compounds due to their similar chemical properties. Analytically pure (A.P.) calcium preparations contain 100–200 ppm of Sr and 30–100 ppm of Ba.

Many methods of separation of strontium and barium from calcium have been described. They are the extractive, the crystallization, the ion exchange, and the precipitation methods. In the majority they relate to those cases where the difference between the concentrations of strontium and barium and the concentration of calcium is not too high /less than 10-100 times/ and in many cases they are not suitable when the microcomponents strontium and barium are to be separated from the macrocomponent calcium.

Some of them (especially the crystallization and the precipitation methods) were used in those cases. Hughs (*1*), for instance, separated strontium and barium by means of tenfold crystallization of calcium sulfate; Angelov et al. (*2*) and Hughs (*1*) used the methods based on the difference of solubilities of Ba, Sr, and Ca hydroxides and oxalates for the preparation of CaO, which was free of spectrographically detectable proportions of strontium and barium. The data shown by the authors were not quantitative. Quantitative data were given by Patti and Hernandez (*3*) who dealt with the preparation of calcium salts with a very low content of strontium. The method was based on the difference of solubility of $Ca(OH)_2$ and $Sr(OH)_2$. By precipitation of calcium hydroxide in a dilute sodium hydroxide solution, small amounts of strontium (1–500 mg) could be separated from large amounts of calcium. The separation yields were determined as a function of the amount of available strontium and the concentration of the sodium hydroxide solution. The method was applied to the preparation of calcium salts with a very low content of strontium (2.9 ppm in relation to Ca).

The aim of this research was to investigate the efficiency of either the hydroxide or the oxalate method in the removal of microamounts of strontium and barium from calcium compounds for the preparation of calcium carbonate with a very low content of strontium and barium.

EXPERIMENTAL

Chemicals (Reagents and Radioisotopes)

Stock solutions: 1 mg/mL of Ba^{2+} and Sr^{2+} as nitrates.

Standard solutions were prepared by suitable dilution of stock solutions and labeling with radioactive isotopes ^{85}Sr and ^{133}Ba supplied by the INR Isotope Production and Distribution Centre Swierk near Warsaw.

Other reagents were of analytical grade (POCh-Gliwice). Some of them were preliminarily purified from Ba and Sr by means of operations described in this paper.

Radioactivity Measurements

The radioactivity of the aqueous phase was measured before and after the operations by means of an LL-1 electronic counter coupled with a GM-meter for liquids, equal volumes (44 mL) of the investigated solution being introduced into the GM-meter.

In the case of ^{133}Ba a NaI(Tl) scintillation counter (EKCO Electronics Ltd., England) was additionally used for measuring radioactivity in the 1 mL aqueous phase.

Procedure

Calculated amounts of $^{85}Sr(NO_3)$ or $^{133}Ba(NO_3)_2$ standard solutions were introduced into 50 mL of 1 *M* $Ca(NO_3)_2$ solution. After measuring the radioactivity (cpm/mL) and the total volume (mL), precipitations of different insoluble salts were carried out. After separation of the precipitates, radioactivity and total volume were measured. Their mean value from three measurements permitted calculation of total radioactivity of the filtrates.

The distribution coefficients $W(\%)$ were calculated according to the following relationship:

$$W(\%) = \frac{\text{total radioactivity in the filtrate after the operation}}{\begin{array}{c}\text{total radioactivity in } Ca(NO_3)_2 \text{ solution}\\ \text{before the operation}\end{array}} \times 100\%$$

The calcium was determined (where necessary) by complexometric titration with sodium versenate.

RESULTS AND DISCUSSION

Coprecipitation of Strontium and Barium with Calcium Hydroxide

Table 1 shows the results of the coprecipitation of strontium and barium with calcium hydroxide in sodium hydroxide solutions. The results indicate that the degree of coprecipitation of strontium and barium is dependent on the sodium hydroxide concentration, the temperature, and the Sr and Ba content in calcium nitrate solution before the operation.

A temperature of 80°C and a decrease of NaOH concentration results in a decrease of the coprecipitated strontium and barium content. The degree of the coprecipitation of strontium and barium drops with a decrease of the content of the elements in calcium nitrate solution before the operation [from 200 (70) ppm to 10 ppm in relation to $CaCO_3$].

An additional investigation concerned with the extraction of calcium hydroxide, obtained by the reaction of calcium oxide with water, by means of hot water. The efficiency of the operation of the removal of strontium and barium from calcium hydroxide was determined spectrographically. The effect of the molar ratio $H_2O{:}CaO$, "α," on the degree of removal of strontium and barium from calcium hydroxide, $R(\%)$, is presented in Fig. 1.

An increase of the molar ratio $H_2O{:}CaO$ is seen to enhance the efficiency of the removal of the elements to about 90%, but for values of α exceeding 30:1 (which relates to a weight ratio of $H_2O{:}CaO = 10{:}1$) the influence is not so distinct as to substantiate the application of a larger excess of water.

Moreover, it has been established that the reactions

$$SrCO_3 + Ca(OH)_2 = Sr(OH)_2 + CaCO_3$$

TABLE 1

Coprecipitation of Strontium and Barium with Calcium Hydroxide Precipitated from 1 *M* Calcium Nitrate Solutions by Means of Sodium Hydroxide

	Coprecipitation of strontium					Coprecipitation of barium				
No.	Temperature (°C)	Sr content before the operation (ppm in relation to $CaCO_3$)	N NaOH[a]	Strontium coprecipitated (%)	Degree of precipitation of calcium (%)	Temperature (°C)	Ba content before the operation (ppm in relation to $CaCO_3$)	N NaOH[a]	Barium coprecipitated (%)	Degree of precipitation of calcium (%)
1	20	200	1.2	10 ± 1.8(2)	99	20	70	1.33	18 ± 1.9(2)	99
2	80	200	0.94	6 ± 1.9(2)	98	20	70	0.93	8 ± 1.8(2)	99
3	80	200	1.9	33 ± 1.9(2)	99	80	70	1.13	2 ± 1.8(2)	99
4	80	10	0.92	19 ± 1.8(2)	98	80	10	0.53	7 ± 1.8(2)	97
5	80	10	1.5	28 ± 1.9(2)	99	80	10	0.87	20 ± 1.9(2)	98

[a] $$N(\mathrm{NaOH}) = \frac{V_{\mathrm{NaOH}} \cdot N_{\mathrm{NaOH}}}{(V_{\mathrm{NaOH}} + V_{\mathrm{Ca(NO_3)_2}})}.$$

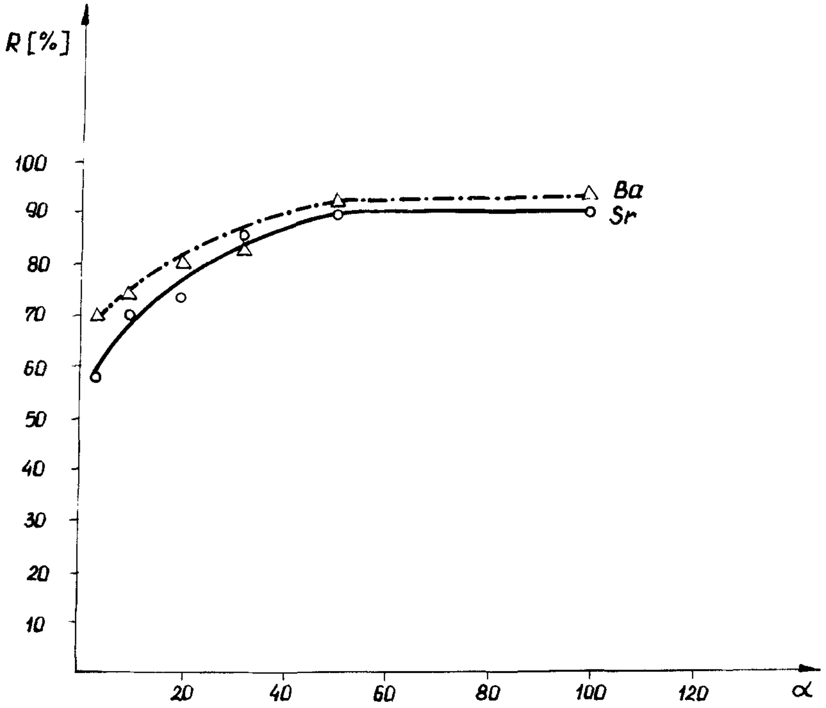

FIG. 1. Effect of molar ratio H_2O:CaO, "α," on the degree of removal of strontium and barium from calcium hydroxide, R(%).

and

$$BaCO_3 + Ca(OH)_2 = Ba(OH)_2 + CaCO_3$$

can partially take place during the extraction of calcium hydroxide with hot water. The removal of strontium and barium is made easier through these reactions. Under conditions of thermal decomposition of calcium carbonate (at about 900°C), strontium and barium carbonates can remain undecomposed because of their higher decomposition temperatures (1290°C for $SrCO_3$ and 1360°C for $BaCO_3$).

The degree of conversion obtained for both reactions under the applied conditions was 40% for Sr and 80% for Ba.

TABLE 2

Coprecipitation of Strontium and Barium with Calcium Oxalate

No.	Content (ppm in relation to $CaCO_3$) before the operation of		Temperature (°C)	*M* $Ca(NO_3)_2$	Molar ratio (Ca^{2+})	Method of precipitation	Molar ratio (CH_3COOH)	Degree of coprecipitation with CaC_2O_4 of		Degree of precipitation of calcium (%)
	Sr	Ba			($C_2O_4^{2-}$)		(Ca^{2+})	Sr (%)	Ba (%)	
1	200	100	20	0.5	1:1	a	—	60 ± 1.8(2)	26 ± 1.7(2)	81
2	200	100	100	0.5	1:1	a	—	38 ± 1.8(2)	14 ± 2.3(2)	79
3	200	—	100	1	1:1	a	—	40 ± 1.8(2)	—	82
4	200	—	100	1	1:1	b	—	41 ± 1.2(2)	—	82
5	200	100	100	1	1:1	c	—	37 ± 3(2)	7 ± 2(2)	83
6	200	—	100	1	1:2	c	—	57 ± 1.8(2)	—	92
7	200	—	100	1	1:1	c	1:1	50 ± 1.8(2)	—	74
8	200	100	100	1	1:1	c	3:1	34 ± 1.8(2)	10 ± 1.7(2)	70
9	10	10	100	1	1:1	c	3:1	39 ± 3.7(2)	5 ± 1.9(2)	70

Coprecipitation of Strontium and Barium with Calcium Oxalate

Calcium oxalate is a slightly soluble calcium compound. Strontium and barium oxalates have somewhat better solubility, especially at high temperatures. Moreover, SrC_2O_4 is slightly soluble in acetic acid.

In these investigations calcium oxalate was precipitated from calcium nitrate solution by means of oxalic acid at 20 and about 100°C. Various quantities of acetic acid were added and three methods of precipitation were used:

(a) Introduction of oxalic acid into the calcium nitrate solution
(b) Introduction of the calcium nitrate solution into the oxalic acid solution
(c) Simultaneous introduction of the calcium nitrate solution and the oxalic acid solution into distilled water.

The results obtained are shown in Table 2.

The data presented indicate that the degree of coprecipitation of strontium and barium depends on the temperature and the excess of oxalic acid. An increase of temperature and a decrease in the excess of oxalic acid cause a drop of the degree of strontium and barium coprecipitation. By precipitation at about 100°C, by means of method "c" and in the presence of an excess of acetic acid, it was possible to achieve the smallest degree of coprecipitation of strontium and barium with calcium oxalate, though the yield of the macrocomponent precipitation was only 70%.

CONCLUSION

Among the methods investigated, the best separation of strontium and barium from calcium was achieved by calcium hydroxide precipitation with NaOH solution and its extraction with hot water.

During the precipitation of calcium oxalate, coprecipitation of the elements took place to a higher degree, particularly in the case of strontium.

The application of both methods of separation of strontium and barium from calcium compounds permitted calcium carbonate preparations containing less than $1 \times 10^{-4}\%$ strontium and barium to be obtained. They were used as the matrix for the determination of strontium in high purity calcium carbonate in a spectrographic method [4].

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