

THE BENEFICIATION OF A VIRGINIA BARITE

by

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## I. INTRODUCTION

The barite industry in the United States started about 1850, but prior to the World War it produced only ground barite and blanc fixe for use in the rubber, paper, and leather industries. The barium chemicals used in this country were nearly all imported from England and Germany, where there are deposits of witherite or nearly pure barium carbonate from which the preparation of barium chemicals is cheap and easy. Practically all barium deposits in this country consist of barite or  $\text{BaSO}_4$  from which the preparation of barium chemicals is rather difficult. In recent years, however, the domestic production of these chemicals has steadily increased. In 1933 5536 tons were produced here while only 757 tons were imported.<sup>1</sup>

There are two common methods for preparing barium chemicals from barite. In the first, cleaned barite is mixed with coal or coke and reduced to the sulfide by roasting in a furnace. The water soluble sulfide is leached out of the mass thus produced, and the solution is then used in the preparation of other barium chemicals. In the second process sodium or calcium chloride is mixed with the barite and coal and this mixture is roasted. The sulfate is converted to the ~~sulfide~~ chloride which may be leached out of the mass. Recently Shreve and Pritchard of Purdue University

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<sup>1</sup> Minerals Yearbook, U. S. Bureau of Mines, 1934

have described <sup>2</sup> a method of producing barium chloride by the action of concentrated calcium chloride solution on barium sulfate

At Austinville, Virginia, there is a deposit of barite on the property of the Bertha Mineral Company. The mineral from this deposit is mixed with rather large amounts of calcite and pyrite and is decidedly off color, hence it is not suitable for grinding to pigment except after difficult and costly purifications and concentration. It should, however, be usable in the preparation of barium chemicals.

The purpose of this investigation was to study the application of the Shreve-Pritchard process mentioned above to the preparation of barium chemicals from the Austinville barite.

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<sup>2</sup> Shreve and Pritchard, Ind. Eng. Chem., Vol. 27, pp. 1488-91

All references to Shreve and Pritchard's work are to this article.

## II., HISTORICAL

As already mentioned, the most generally used methods for decomposing barium sulfate so as to obtain soluble barium compounds consist of furnace reductions. Various authors have also described methods of decomposing barium sulfate by heating with alumina or silica.

The fact that barium sulfate could be decomposed by means of calcium chloride in concentrated solutions appears to have been discovered by Still at Purdue University while working under Shreve in 1932. He proved that the reaction between barium chloride and calcium sulfate could be reversed under conditions of high concentration and temperature. A more detailed study of this reaction was then made by Shreve and Pritchard who brought the work up to its present point.

## I II. EXPERIMENTAL

### 1. Analysis of Raw Material:

The original sample of mineral sent to the V.P.I. Department of Chemical Engineering by the Bertha Mineral Company was found to be entirely unlike barite both in appearance and specific gravity. It was further found that this mineral was 94.67% soluble in hot 1:1 hydrochloric acid. No trace of soluble barium was found in the solution. Further analysis showed that the mineral contained 92%  $\text{CaCO}_3$  and 1.65%  $\text{Fe}_2\text{O}_3$ . It was therefore concluded that a limestone had been mistaken for barite by the mineral company.

### 2. Preparation of a Modified Sample:

A large lump of a mineral which had been taken from the Austinville property and which was unquestionably barite of a good grade was, however available. This mineral was found to be but 2.3% soluble in hydrochloric acid. Some of it was crushed to -60i-80 mesh and a representative sample of this was taken. In order that the tests of the Shreve-Fritchard process might be made on a barite of as poor or poorer quality as any likely to be mined at Austinville, a mixture of 3 parts of the good grade barite with 1 part of the limestone described above was made. All tests of the process were then made on this mixture

### 3. Tests:

Two series of tests of the Shreve-Pritchard process were made on the barite-limestone mixture as follows:

Series 1: The same weight of barite heated under identical conditions with different weights of calcium chloride.

3 grams of the barite-limestone mixture were weighed out into each of six 300 cc. Erlenmeyer flasks, and 4.5 cc. water was added to each flask. A weighed amount of dry calcium chloride was also added to each according to the following schedule:

Flasks Nos. 1-A and 1-B ----- 5 grams  $\text{CaCl}_2$

Flasks Nos. 2-A and 2-B ----- 6 grams  $\text{CaCl}_2$

Flasks Nos. 3-A and 3-B ----- 7 grams  $\text{CaCl}_2$

Each flask was then stoppered with a cork pierced with a short glass tube having a fine capillary opening and all were placed in an oven at  $80^\circ \text{C}$ . After 24 hours the contents of the flasks were nearly dry, and 4.5 cc. more water was added to each. After 24 hours more in the oven, the flasks were removed and their contents analysed for barium chloride.



Series 2: Different reaction mixtures evaporated to dryness different numbers of times at 105° C.

3 grams of barite-limestone mixture and 4.5 cc. of water were added to each of six 300 cc. Erlenmeyer flasks. Dry calcium chloride was then added to each of the flasks according to the following schedule:

Flask No. 4	-----	5 grams CaCl <sub>2</sub>
Flask No. 5	-----	6 grams CaCl <sub>2</sub>
Flask No. 6	-----	5 grams CaCl <sub>2</sub>
Flask No. 7	-----	6 grams CaCl <sub>2</sub>
Flask No. 8	-----	5 grams CaCl <sub>2</sub>
Flask No. 9	-----	6 grams CaCl <sub>2</sub>

The flasks were not corked and were put in an oven at 105° C. where they were left until their contents had evaporated to dryness. This took about four hours. Flasks Nos. 4 and 5 were then removed for analysis. 4.5 cc. of water were added to each of the other flasks and they were allowed to remain in the oven until their contents had evaporated to dryness a second time. After the second evaporation Flasks Nos. 6 and 7 were removed for analysis, and 4.5 cc. of water were added to Flasks Nos. 8 and 9. After a third evaporation Flasks Nos. 8 and 9 were removed for analysis.

#### 4. Method of Analysis of Reaction Mixtures for Barium Chloride:

The reaction mixtures were after the procedure given by Shreve and Pritchard, with some slight modifications.

To the contents of each reaction flask were added 100 cc. of ethylene glycol-methanol solution ( 1 volume ethylene glycol to 3 volumes methanol). The solvent was allowed to stand in contact with the reaction mixture for at least 24 hours, after which time the solution was filtered off through a qualitative filter paper into a 250 cc. volumetric flask. The residue on the filter was then washed with 25 cc. of the solvent. The contents of the volumetric flask were diluted to the mark and mixed thoroughly.

100 cc. of the solution was then transferred from the volumetric flask to a 400 cc. beaker by means of a pipette. This solution was diluted to 250 cc. with water and 6 drops of acetic acid were added. The solution was then heated to boiling.

The barium in the solution was then precipitated by adding 15 cc. of 10% ammonium chromate solution drop by drop with constant stirring. By adding the chromate solution very slowly with the barium solution just at the boiling point, but not actively boiling, a rapid settling non-creeping precipitate of barium chromate was obtained. The solution was allowed to stand after precipitation just

long enough for the precipitate to settle. If the solution was allowed to stand longer than one hour it was oxidized and the determination was spoiled.

After the precipitate had settled, as much of the clear solution as possible was decanted through a Gooch crucible. The filtrate was discarded, and the residue in the crucible was dissolved into a clean filter flask with 20 cc. of hot 5% nitric acid. The hot acid filtrate was poured back into the beaker containing the bulk of the precipitate, and the flask was washed out into the beaker with 200 cc. of water. The nitric acid gradually dissolved the precipitate in the beaker.

The solution in the beaker was then heated just to boiling, made alkaline with 1:1 ammonium hydroxide, then acid with acetic acid. 15 cc. of ammonium chromate solution was then added exactly as in the first precipitation. The precipitate of barium chromate produced was allowed to settle. It was then filtered off in a weighed Gooch crucible, washed with water, and dried to constant weight.

The weight of barium chromate obtained multiplied by 2.5 and by the proper gravimetric factor gave the weight of barium chloride in the reaction mixture.

5. Results of Experimental Work:

TABLE I

Results of heating equal weights of barite with different weights of calcium chloride under identical conditions:

No.	grams barite used	grams CaCl <sub>2</sub> used	cc. water used	Treatment	Grams BaCl <sub>2</sub> produced
1-A	3	5	4.5	Heated at 80° C for 48 hours	1.4562
1-B					
2-A	3	6	4.5	Same as 1	1.2782
2-B					
3-A	3	7	4.5	Same as 1	1.2201
3-B					

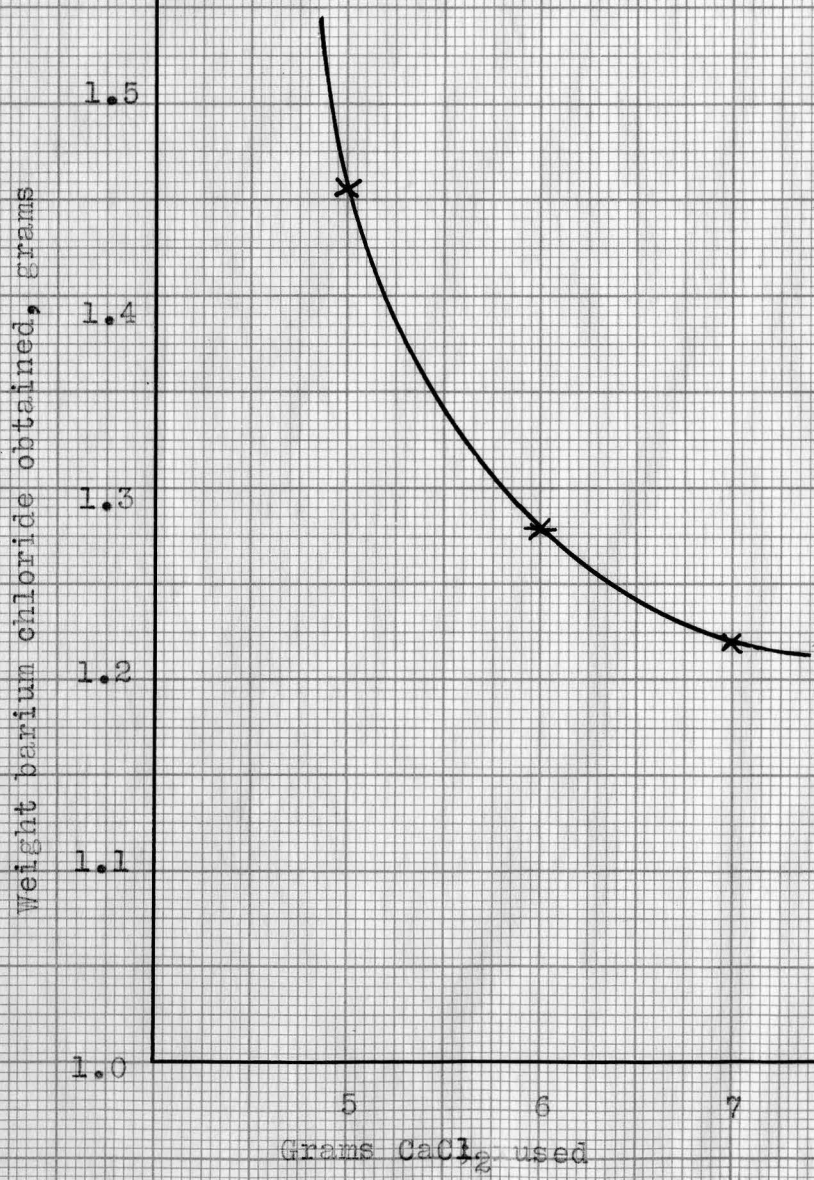
TABLE II

Results of evaporating reaction mixtures of various compositions to dryness various numbers of times at 105° C.:

No.	grams barite used	grams CaCl <sub>2</sub> used	cc. water used	Treatment	grams BaCl <sub>2</sub> produced
4	3	5	4.5	Evaporated to dryness once at 105°C.	0.3321
5	3	6	4.5	Same as 4.	0.3298
6	3	5	4.5	Evaporated to dryness twice	0.5549
7	3	6	4.5	Same as 6.	0.5413
8	3	5	4.5	Evaporated to dryness three times	0.7822
9	3	6	4.5	Same as 8.	0.7436

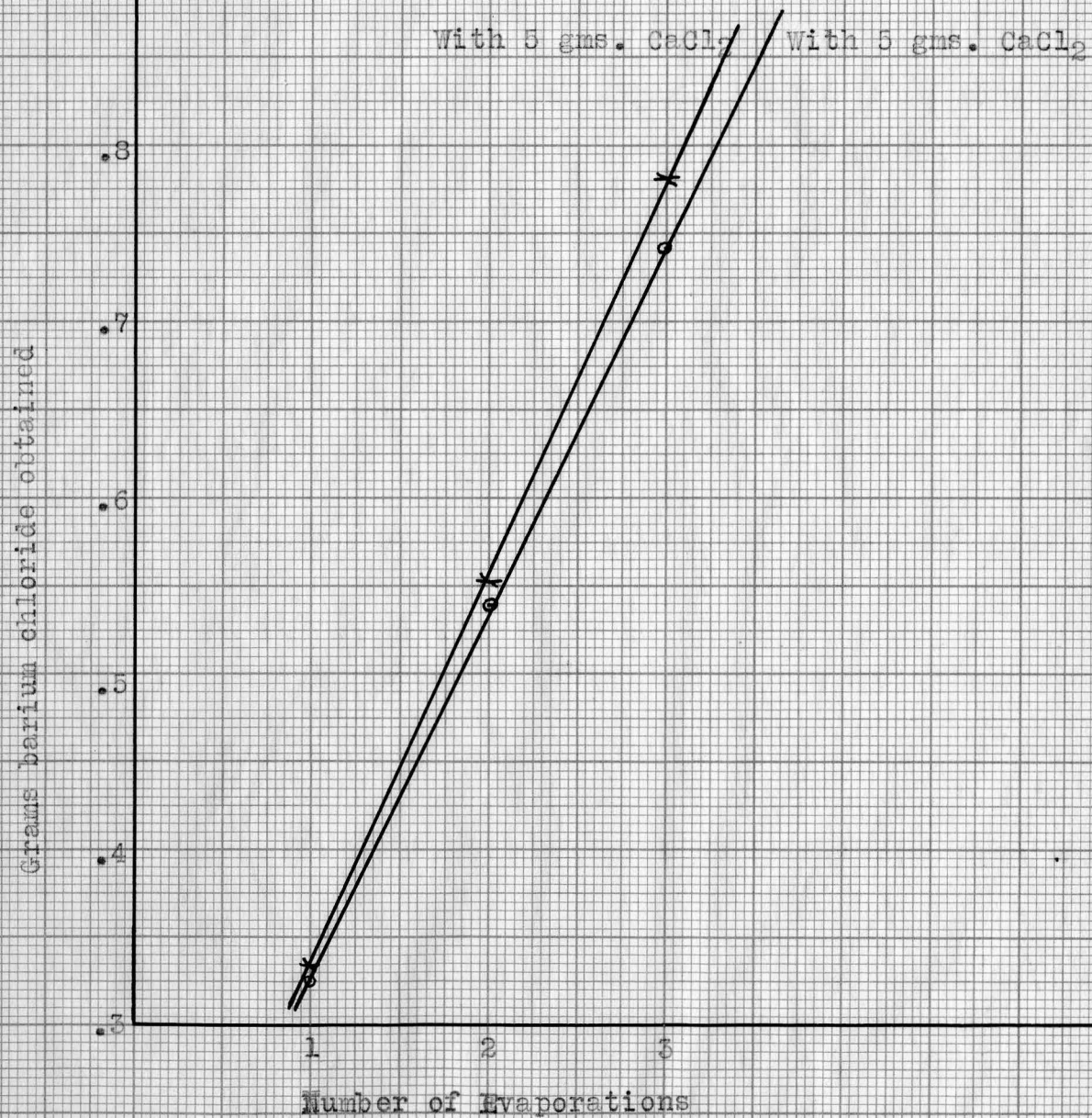
Curve No. 1

Showing the weights of barium chloride obtained by treating 3 grams of crude barite with different weights of  $\text{CaCl}_2$



Curve No. 2

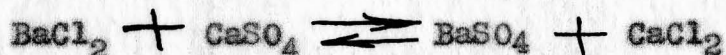
Showing the weights of barium chloride obtained by treating 3 grams of crude barite with equal weights of calcium chloride and evaporating to dryness different numbers of times.



#### IV. DISCUSSION

##### 1. General:

The results obtained in the experimental work which has been described on previous pages of this report show that the reaction:



which is generally considered to be irreversible, may be reversed in concentrated solutions. They also show that reversal of this reaction is possible not only with pure chemicals as was shown by Shreve and Pritchard, but also with a very crude barite containing relatively large amounts of calcium carbonate and iron. The results fail, however, to show the conditions of reaction and the proportions of the reacting materials which will give the best conversion of the barite to the chloride.

##### 2. The Effect of the Rate of Evaporation of the Reaction Mixture:

The large difference in the amounts of barium chloride obtained in the first and second series of tests show that conversion is more rapid and more nearly complete when the reaction mixture is heated under conditions such ~~that~~ that the water evaporates very slowly than when it evaporates rapidly, the total time of reaction in each case being the same.



3. The Effect of the Amount of Excess Calcium Chloride Used on the Amount of Conversion Obtained:

The results obtained in both series of tests show that increasing the amount of excess calcium chloride used in the reaction mixture causes the amount of conversion obtained to be decreased.

4. The Law of Mass Action Does not Apply:

If the reaction:



were a normal reversible reaction, increasing the amount of excess calcium chloride would displace the equilibrium toward the left in accordance with the law of mass action and would hence increase the amount of barium sulfate converted to the chloride. The results obtained show, however, that within the limits of this experiment just the reverse is true. These results are contrary not only to the law of mass action but also to the results obtained by Shreve and Pritchard while working on the same system. That the results obtained here are due to experimental errors seems unlikely in light of their uniformity and the fact that in the first series of tests all results given are the average of closely checking duplicates.

5. Commercial Aspects of The Shreve-Pritchard Process:

Naturally much work must still be done before it can be definitely determined whether or not the Shreve-Pritchard process can be put on a paying commercial basis. If an attempt is made to apply it to the production of

pure crystalline barium chloride difficulty in separating the barium chloride from the calcium chloride present in the reaction mixture may be encountered. The reaction mixture should, however, be suitable for use in the preparation of blanc fixe. Upon dilution of this mixture and addition of the sulfate ion to it barium sulfate will be precipitated. Any calcium sulfate precipitating may be readily dissolved out with water.

6. The Application of the Process to the Case of the Bertha Mineral Company:

If it should later be found that the Shreve-Pritchard process is commercially feasible, the Bertha Mineral Company seems to be in an ideal situation for using it. They have the barite, calcium chloride is available from Saltville at very small cost, and coal for heating is abundant and cheap. Besides, if their barite is of a low grade as it appears to be, the Shreve-Pritchard process can be applied where a furnacing method cannot.

## V. CONCLUSIONS

On the basis of the results obtained in the tests made on the Shreve-Pritchard process for producing barium chloride from barium sulfate the following conclusions are made:

1. Barium chloride may be produced from barium sulfate by treatment with calcium chloride in concentrated solutions.
2. It may even be produced from a barite of as low or lower quality than any ~~xxxxxxxxxxxx~~ usually mined.
3. Within the limits of these tests, increasing the amount of excess calcium chloride in the reaction mixture causes the amount of conversion obtained to be decreased, i. e. the law of mass action does not apply in this case.

## VI. SUMMARY

Two series of tests were run on the conversion of a modified sample of the Austinville barite to the chloride by the action of concentrated calcium chloride solution. In the first series barite, calcium chloride, and water in various proportions were mixed and heated in an oven at 80° C. for 48 hours. In the second series the reaction materials were evaporated to dryness varying numbers of times in an oven at 105° C.

From a 3 gram sample of barite from 1.4562 to .3321 grams of barium chloride was obtained, the amount depending on the conditions and proportions used in the reaction.

The effect of the amount of excess calcium chloride used upon the amount of chloride obtained was indeed unusual. Contrary to the law of mass action, it was found that the greater the excess of calcium chloride used the smaller was the amount of barium chloride obtained. This condition was encountered in all of the tests made.

## VI. SUGGESTIONS FOR FUTURE WORK

In case any experimenter should continue the work on the problem of preparing barium chloride from barium sulfate by the action of calcium chloride, it is suggested that he obtain data to extend Curve 2 on page 13 of this report, especially to the left. This curve must eventually show a maximum point which will fix the proportion of calcium chloride giving the best conversion. Also a study of the effects of agitation, reaction temperature, and time of reaction on the amount of conversion would be desirable

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