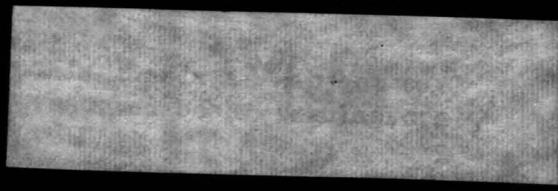
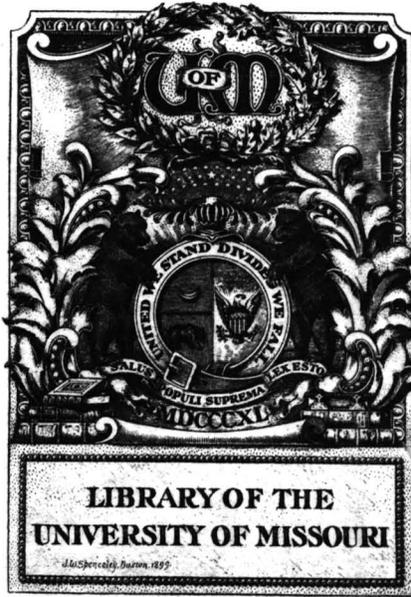


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THE EXTRACTION AND RECOVERY OF RADIUM
FROM LOW GRADE AMERICAN
PITCHBLEND E ORES

by

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SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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*Reads Approved
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THE EXTRACTION AND RECOVERY OF RADIUM
FROM LOW GRADE AMERICAN
PITCHBLENDE ORES

CHAPTER I. INTRODUCTION

A. Source of Ore

The pitchblende deposits of the United States are widely distributed, altho the most extensive deposits are found in Colorado. In the past many of them have yielded ore carrying high percentages of uranium oxide (U_3O_8), sometimes as high as 80 per cent U_3O_8 . Consequently only these were utilized and the low grade ores, which contained very high percentages of iron pyrites with correspondingly low percentages of U_3O_8 , were thrown on the dump. ⁽¹⁾ Since this rejected ore is much larger in amount than the rich ore, a method of recovering the wasted radium and uranium is desirable.

B. Concentration of Ore

Where the low grade ore is utilized at all, the method of concentration is as follows:

The ore is hand-sorted to remove as much waste rock as possible, then crushed, sized and classified. Ore of the desired mesh is treated with water and spread out on sludge

(1) U.S. Bur. of Min. Bul. 70. p.43 et seq.

tables. A great part of the matrix is separated in this way but no amount of sorting and mechanical grinding or even fine crushing with subsequent flotation serves to separate the radium-bearing mineral from the accompanying pyrite. Evidently the pitchblende must be held in solid solution by the pyrite. By sampling and concentration at the mill, the ore is divided into three grades----high-grade, containing upwards of 16 per cent U_3O_8 , medium-grade, containing right around 4 per cent U_3O_8 , and low-grade, containing less than 2 per cent U_3O_8 .

C. Description and Composition of Ore

The ore used in the experiments outlined below was the low-grade ore and was furnished from one of the Gilpin county, Colorado mines by Dr. R.B. Moore of the United States Bureau of Mines. It had been ground to pass a 20-mesh sieve. In all of the preliminary experiments it was not further ground. In the chlorination experiments described in the second part of this thesis, it was ground to pass an 80-mesh sieve.

While no attempt was made at either a complete qualitative or quantitative examination of this ore, it may safely be said to contain about 85--90 per cent iron pyrites, a small quantity of copper pyrites, and 7-15 per cent silica. An assay of the ore shows it to contain 3.43×10^{-9} grams of radium per gram, which corresponds to 1.3 per

(2)
cent of U_3O_8 .

D. The Problem

Thus these pitchblendes differ considerably from the European pitchblendes, which contain no iron pyrites and can be easily dissolved with dilute sulfuric acid after fusion of the ore with sodium sulfate, when the radium is left in the residue. (3) They are also unlike the high-grade pitchblendes produced in this country which are readily soluble in nitric acid. Bulletin 104 of the United States Bureau of Mines states, "High-grade pitchblende is low in silica and readily soluble in hot 1:1 nitric acid." (4) The ore used in the experiments described in this thesis can also be dissolved by hot 1:1 nitric acid but only after all the sulfur of the pyrites has been oxidized by the acid. Since the amount of nitric acid required is enormous, and the recovery of radium rarely exceeds 60 per cent, this is obviously too expensive a method for an ore of such indifferent value.

The problem then is to find a comparatively inexpensive substitute for the nitric acid method of extracting radium from low-grade pitchblendes and at the same time to secure a higher recovery of radium. To attain these ends, experiments were devised to eliminate sulfur from the ore. This thesis (1) describes some of the methods by which sul-

(2) U_3O_8 was not determined directly, but calculated by multiplying the amount of radium as determined by the emanation method by 3×10^6 . This is the accepted constant for the ratio of uranium to radium in primary uranium minerals.

(3) U.S. B. Of Mines, Bul. 70. p. 79.

(4) U.S. B. of Mines, Bul. 104. p. 98.

fur was eliminated from the ore; (2) describes the results of various methods of treatment of the desulfurized ore; (3) presents a new method of treating this ore, namely, by chlorination, which resulted in a high extraction and an easy recovery of the radium; (4) gives a quantitative analysis of the chlorination method; and (5) gives a quantitative distribution of the radium among the various products obtained by the chlorination method.

In the work described in the succeeding pages, much in the way of suggestion on methods and help in the manipulation of electroscopes was given by Dr. Herman Schlundt, for which grateful acknowledgement is here made.

CHAPTER II. PRELIMINARY AND QUALITATIVE WORK

Experiments in which the original ore was treated directly with acids show a low extraction with high consumption of acid. ⁽¹⁾ In the hope of making an easy extraction by eliminating the sulfur from the concentrate before giving the acid treatment, the ore was roasted to the oxide.

A. Work on the Roasted Ore

For this experiment a sample of low-grade ore was roasted in an open muffle for $7\frac{1}{2}$ hours without stirring. ⁽²⁾ The roasted ore seemed to be thoroly converted to the oxide of iron, but possibly was a mixture of different oxides, since the color was not uniform. The following data record the results of this experiment:

Weight of Ore-----	273 grams
Length of Roast-----	$7\frac{1}{2}$ hrs.
Weight after roasting-----	200 grams ⁽³⁾
Activity of original ore-----	.0846 dps.
Activity of Roasted Ore Immediately-----	.0486 dps.
Apparent Loss of Activity -----	43.6%
Activity of Roasted Ore After One Week--	.0468 dps.

(1) Dr. Herman Schlundt, Unpublished results. Some of these show that 1560 pounds of HNO_3 to the ton of a low-grade ore extracted only 26% of the radium. When this residue was boiled with concentrated H_2SO_4 twice, only 3% of radium was in the tailings.

(2) Ibid. Dr. Schlundt shows that the greater the amount of roasting the smaller the residues left on treatment with acid.

(3) dps.--abbreviation for divisions per second; showing the discharge of an electroscope expressed in arbitrary units.

The alpha ray radiation for the roasted ore seems to be abnormally small. The question arises as to whether some of the radium has not been lost thru vaporization. This result confirms work of a similar nature done by Dr. Schlundt and described by him in some unpublished papers. His results indicate that the greater the amount of oxidation the greater the apparent loss of activity of the roasted ore. His further experiments show that in later treatment of the roasted ore with acids the radium had not been lost but was still in the ore and later exhibited itself in a full activity.

1. Fusion of Roasted Ore with Nitre Cake

Believing that fusion with nitre cake might result in the formation of the sulfates of iron, which could be easily dissolved out in water, 10 grams of the roasted ore were melted in an iron dipper with three times its weight of nitre cake over a Bunsen flame and kept fused at the lowest possible temperature with constant stirring for about five minutes. The mass was then poured into a vessel of water. A small amount of ferric sulfate was dissolved in the water, but the main part of the iron was precipitated again as red ferric oxide (Fe_2O_3) or a mixture of Fe_2O_3 and Fe_3O_4 . A blank was run with ferric oxide from the storeroom with the same results. No measurements were made of the activity

of the large residue from this treatment, since the method is evidently impracticable.

2. Treatment of Roasted Ore with Concentrated Sulfuric Acid

9.45 grams of roasted ore were digested with concentrated sulfuric acid in the cold for two weeks, then boiled a few minutes. The liquid was poured off into a large volume of water. The residue was covered with more acid and boiled quietly for about 30 minutes. Then this liquid was poured into the water with the first. After filtering and drying, the residue was found to have an activity of .0738 dps. This means that 63% of the radium is present in the residue, while only 37% was extracted by the acid. As this extraction was less than had been expected, no further work was done on this method.

3. Fusion of Roasted Ore with Salt and Lye

9.5 grams of roasted ore were fused with 20 grams of salt and 4 grams of commercial lye. (4) The mass was extracted with water and filtered. The dried residue had an activity of .0416 dps. This shows an extraction of only 11% of the roasted ore. So unfavorable an extraction did not warrant further work in this direction.

(4) Commercial lye contains 75% NaOH, 20% NaCl and 3% Na₂CO₃.

B. Work on Reduced Ore

Owing to the unsatisfactory results obtained in the work described above, experiments on the roasted ore were discontinued and attention was given to reducing the roasted ore and experimenting with the product. Previous experiments conducted by Dr. Schlundt in which a pitchblende was given a direct reducing roast resulted in a fair separation of the sulfur, but in an unprofitable extraction of radium with acids, when the relatively large amounts of acid required were considered. (5) Accordingly only roasted ore was used in these reduction experiments.

About 300 grams of the roasted ore were placed in a 1-inch steam pipe in a combustion furnace and coal gas passed over it at a red heat for about 8 hours. This was probably twice as long as necessary, since, after the first three hours of heating, steam ceased to be given off. The iron of the pipe reacted to some extent with a small amount of sulfur, left in the roasted ore, to form a scale of ferrous sulfide. Since efforts to separate this scale were unsuccessful, no weighing of the reduced ore was made. A rough calculation based on the amount of sand residues left on treatment of the reduced ore with acids put the weight of reduced ore at about 146 grams. (6) The reduced ore was a

(5) Dr. Herman Schlundt, Unpublished papers.

(6) 4.17 grams of tailings were left from 31 grams of the reduced ore on treatment with H_2SO_4 followed by HNO_3 . Altho it must be borne in mind that the roasted ore still contained a small quantity of sulfur, which formed a scale with the iron of the reduction tube, and that the oxide was not

dull black in color and had much the appearance of metallic iron.

This reduced ore was passed thru a 20-mesh sieve to remove as much scale as possible before the following data were taken:

Activity of original ore-----	.0846 dps.
Activity of roasted ore immediately-----	.0486 dps.
Activity of roasted ore after 1 day-----	.0468 dps.
Activity of reduced ore after 4 days-----	.0701 dps.
Activity of reduced ore after 6 days-----	.0898 dps.

But the reduced ore weighs approximately only 53.5% of the original ore taken to obtain it. Therefore the radium in the reduced ore is 56.7% of the whole, i.e. the reduced ore has not as yet recovered all of its activity. After 6 days, it is weight for weight 1.061 times as active as the original ore.

1. Treatment of Reduced Ore with Sulfuric Acid

Followed by Nitric Acid

31 grams of the reduced ore were treated with 450 grams of sulfuric acid(2:7).⁽⁷⁾ The action was carried on in the cold for two hours, then heated gently and finally kept boiling until the slight odor of hydrogen sulfide,

necessarily all ferric oxide, it may be assumed for a rough calculation that the sulfur and other oxides of iron may be neglected. Then the 31 grams of reduced ore represents 42.5 grams of roasted ore and the reduced ore from 200 grams of roasted ore equals 146 grams of reduced ore.

(7) The amount of H_2SO_4 used was a great deal larger than necessary. In order to insure complete decomposition, it was added as the odor of H_2S persisted. The sample was probably mostly dissolved long before the odor of H_2S disappeared.

which accompanied solution of the ore, was lost. Filtration left a black residue which was treated at once with nitric acid (1:4). This gave a green solution and a residue apparently made up of sand and a black powder. It is probable that another extraction might have dissolved out the rest of the black powder, which doubtless contained most of the remaining radioactive material. Examination of this residue gave the following results:

Weight of sample of reduced ore -----	31 grams
Weight of sulfuric acid used-----	447 grams
Weight of residue -----	4.17 grams
Per cent of residue (of reduced ore)----	13.4%
Per cent of residue (of original ore)---	7.1%
Per cent of radium in tailings -----	36.2%
Per cent of radium extracted-----	63.8%

Since the clear sulfuric acid solution would be very unlikely to contain any of the radium, the green nitric acid solution was examined. This solution was left standing in the laboratory for some days when a small amount of finely divided white precipitate appeared. This was filtered off and found to have an activity of 1.337 dps. or to be weight for weight 15.8 times as active as the original ore. The solution from which the above precipitate was removed was again left standing in the laboratory for several weeks when it again threw down a small white precipitate which had an activity of .4361 dps. or 5.15 times as much as the original ore. These two precipitates were combined and ignited but were lost before a weighing could be made.

Doubtless the sulfuric acid converted the radium

into the insoluble sulfate, which was later dissolved in the nitric acid, and afterwards carried down on dilution of the solution with washings. This experiment gives no idea of the amount of material extracted by the sulfuric and nitric acids respectively. To determine this, 37 grams of the reduced ore were heated with 40 cc. of concentrated sulfuric acid diluted with 100cc. of water. It was allowed to stand in the cold for 18 hours and then heated gently for four hours. When action ceased, it was filtered and the residue ignited and found to weigh 8.51 grams or 23% by weight of the reduced ore. This residue was covered with 25cc. of concentrated nitric acid, ⁽⁸⁾ heated for a few minutes, and the acid decanted with suction thru a Büchner funnel, covered with an asbestos cloth. The residue was again covered with 25 cc. of concentrated nitric acid, boiled a few minutes and decanted thru the same funnel. The residue was covered with 20cc. of cold concentrated nitric acid and allowed to stand for a few days. The liquid was filtered by suction thru a Büchner funnel and washed with HNO_3 (1:2), and distilled water. The precipitate was brown in color, and contained a good deal of silica. As it could not be completely freed of shreds of asbestos, the residue was not weighed. If in line with the preceding experiment, about 10% was extracted by the nitric acid. Its activity was .1785 dps. or 2.1 times as active as the original ore.

(8) The residue seems to be made up of many things, chief among which is a very black precipitate, a brown precipitate, and a quantity of silica.

The filtrate and washings were combined and a few drops of barium chloride and sulfuric acid added to them. The precipitate was filtered after standing in solution three days, dried, and its activity measured by the film method. It was found to be 7.36 times as active as the original ore. It will be noticed that this figure is not so high as that obtained in the preceding experiment. This is due to the fact that a comparatively large excess of barium chloride was used in the precipitation while in the other the precipitate was not brought down by added barium chloride -----the base of that sulfate precipitate was present in the original ore.

In order to see how much radium remained behind in the nitric acid solution of the preceding experiment, the whole filtrate was evaporated to dryness and the activity of the residue measured by the film method. This was .0369 dps.

Below are summarized the activities of various products of this method. Since no weighings were made, except on the tailings, it is impossible to present even a rough balance sheet.

Activity of original ore-----	.0846dps.
Activity of roasted ore -----	.0486 dps.
Activity of reduced ore-----	.0898 dps.
Activity of tailings -----	.2416 dps.
Activity of first precipitate from HNO_3 sol.	1.337 dps.
Activity of second precipitate from HNO_3 sol.	.4361dps.
Activity of reidue from evap'n of HNO_3 sol.	.0369dps.
Activity of crude Ba-RaSO_4 from HNO_3 sol.	.6217dps.

3. Reduced Ore Treated with Hydrochloric Acid

23.45 grams of reduced ore were treated with 30 grams of hydrochloric acid. When decomposition was complete, the residue was filtered off, washed with boiling water, ignited, and weighed. It was found to weigh 4.00 grams, i.e. 18% of the sample taken. The residue was brick red in color, altho it contained much sand. It had an activity of .2383 dps. 47.26% of the radium was left in the tailings and 53% was extracted. Barium chloride solution and sulfuric acid were added to the filtrate. The activity of the dried sulfates was .1653 dps.

The extraction of radium from reduced ore by means of acids may be summed up as follows:

Reduced ore with H_2SO_4 and HNO_3 -----	63.8%	
Reduced ore with H_2SO_4 and more HNO_3 ---	73%	(9)
Reduced ore with HCl -----	53%	

The above extraction figures must be regarded as only roughly quantitative, since all activities were measured by the alpha-ray method. The values found for these activities are not really comparable, since it was not possible to make readings at definite intervals after precipitations and extractions were made. Consequently the accumulation of the short-lived disintegration products of radium,-----Radium A,

(9) Since no weighing was made in the second experiment, where the reduced ore was first treated with H_2SO_4 and then with HNO_3 , the weight of the residue was calculated from the per cent of residue left in the first experiment and the per cent of radium extracted was calculated from the figure so obtained.

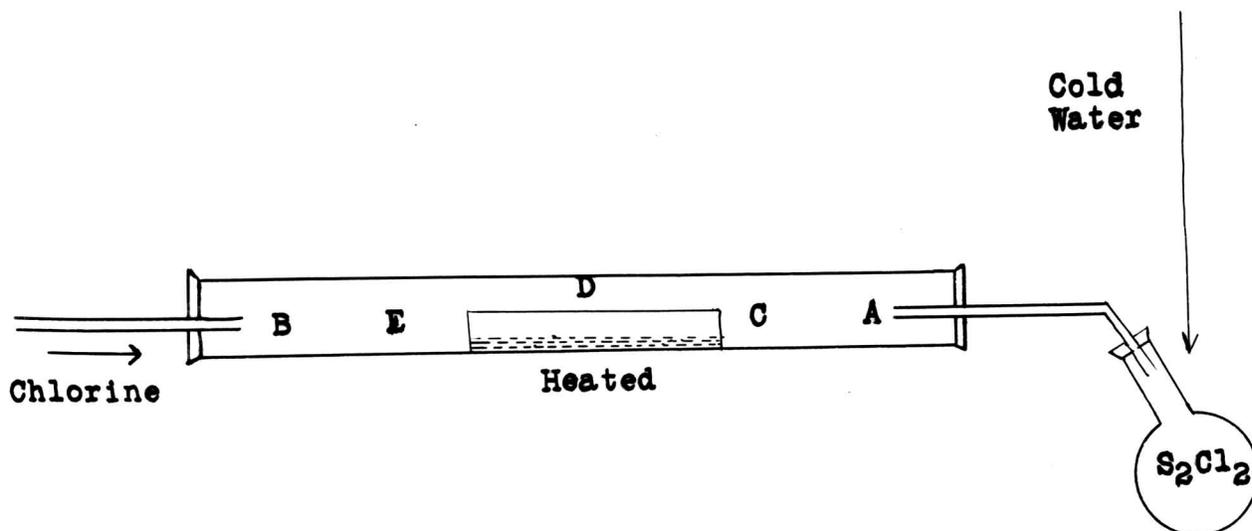
Radium B, Radium C, Radium Emanation---which produce a steady rise in the alpha-ray activity of radioactive substances for a month following precipitation, was in no two cases the same.

While the above qualitative experiments show that a fair extraction is possible, the process is made up of so many steps----roasting, reducing, and use of large quantities of acids, with no possibility of any considerable recovery from by-products---that a simpler means of extraction, involving fewer steps, would be more desirable. An effort in this direction is made in the experiments next recorded.

C. Preliminary Chlorination Experiments

Upon first that it was believed that if chlorine were passed over the heated ore it would combine with the sulfur and iron of the ore, forming sulfur monochloride (S_2Cl_2) and ferric chloride ($FeCl_3$) and leaving the radium in the tailings, from which it could be removed without great difficulty.

The first experiment was a very simple qualitative one. The coarse ore was placed in a short, heated glass tube and chlorine passed over the red hot ore. The operation took less than half an hour, and the accumulation of $FeCl_3$ at the cooler end of the tube finally stopped up the tube. The pressure of the chlorine forced it and the connection leading to the container in which the sulfur monochloride



A and B----Black crystals, probably $FeCl_3$.
 C and E----Probably a mixture of $FeCl_2$ and $FeCl_3$.
 D-----Tailings or unattacked residue.

PLATE I.

Diagram of Apparatus Used in Preliminary
 Chlorination Experiment

was being collected. At first it seemed practicable to keep the different products of chlorination separate just as they were formed in the tube. (See Plate 1.)

Each of these products was examined electroscopically by the film method with the following result:

Activity

A and B-----	.0175 dps.
C and E-----	.0444 dps.
D, Tailings-----	.0603 dps.
Original Ore-----	.1177 dps. (10)

These figures appear to show that most of the radium remained in the tailings, except such of it as is carried over by mechanical means to the portion of the tube next adjoining. In order to confirm this, all the products of chlorination were collected together and boiled with water. The hot water filtrate was evaporated to dryness---- the residue showed an activity in 5 days of .0693. The portion undissolved in hot water was boiled with a small amount of hydrochloric acid, giving a greenish yellow solution. This was filtered off and evaporated to dryness. It showed an immediate activity of .0350 dps. and an activity after 5 days of .0339 dps. The residue from the hydrochloric acid treatment seemed to be a mixture of silica, sulfur, and unattacked ore. This fact indicated that there must be a slower and longer chlorination. This residue was ignited

(10) This figure is not the same as that given in an earlier part of the paper for the activity of the original ore, since the capacity of the measuring electroscopical was altered in the meanwhile.

to get rid of the sulfur. It had an immediate activity of .0322 dps. and after 5 days of .0325 dps.

	Activity	Weight	Radium present
Original Ore-----	.1177-----	6.85 g.	
Res. from evap'n of Aq. sol.--	.0693		
Res. from evap'n of HCl Sol.--	.0339		
Tailings -----	.0325-----	1.415-----	5.5%
Radium extracted-----			94.5%
Crude sulfates-----	.1336		

The figure given above for the radium present in the tailings is obtained in the following way: The total activity of the tailings is found by multiplying the weight of the tailings, 1.415 grams, by the rate at which the alpha-ray electroscope was discharged, .0325 dps., or .0460. Similarly the total activity of the ore was found to be .8062. Then the percentage of radium left in the ore is represented by $\frac{.0460 \times 100}{.8062}$, or 5.6%. The percentage of radium extracted is found by difference.

The above results show that the greater part of the radium is not present in the tailings, as first supposed, but in that part of the product which is soluble in water and hydrochloric acid. The amount of hydrochloric acid required for solution is very small, as is also the quantity of material dissolved by the hydrochloric acid alone. The percentage of radium in the tailings would obviously be still further reduced by more thorough chlorination. The figure

for the crude sulfates given above was obtained by combining the residues from the evaporation of the solutions in water and hydrochloric acid, redissolving in water and dilute hydrochloric acid and precipitating with barium chloride solution.

The high percentage of radium extracted gives promise of very favorable results under more careful control of chlorination, and justifies further experiments, which will now be described.

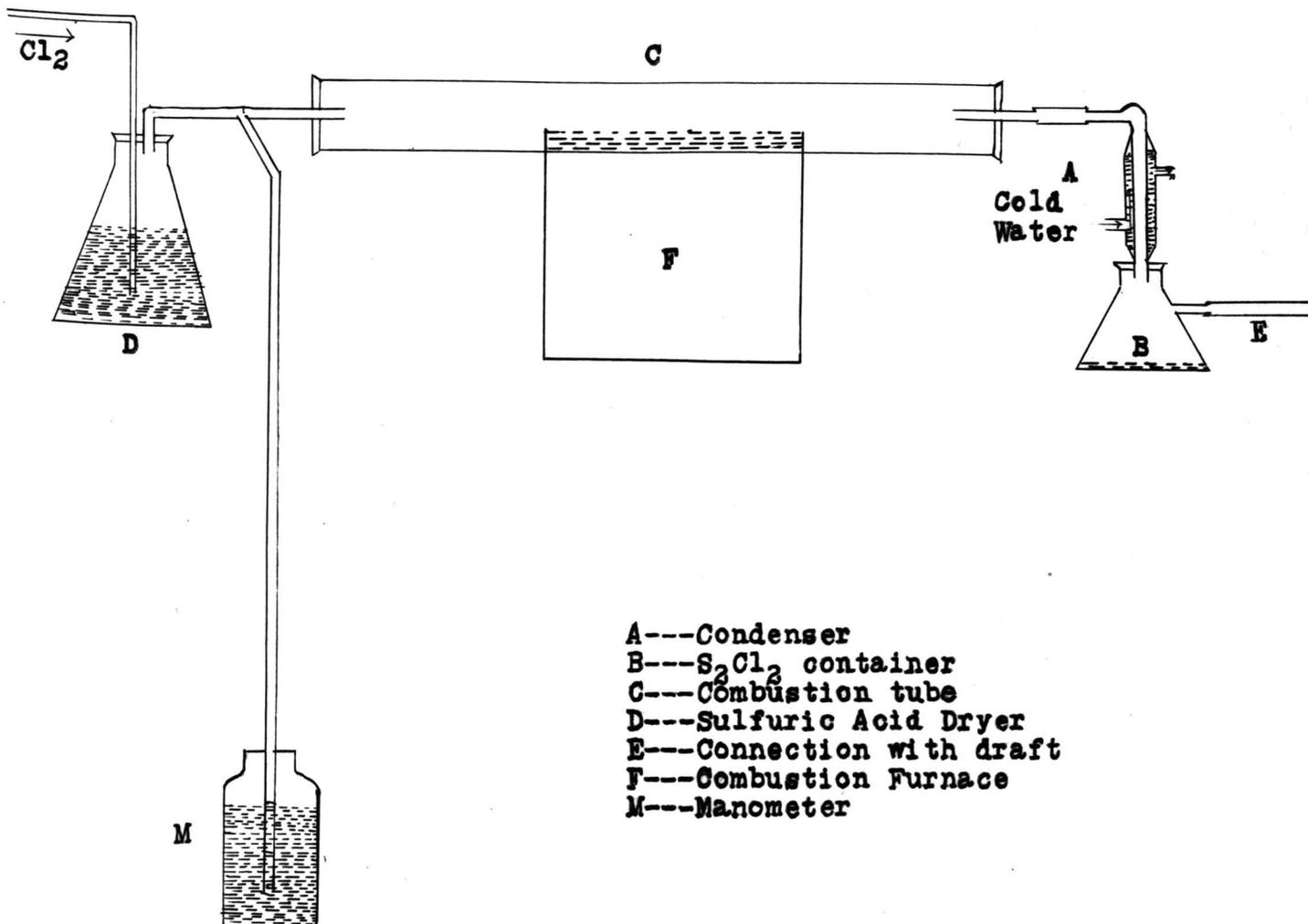


PLATE II.

Diagram of Apparatus Used in Final
 Chlorination Experiment

III. EXTRACTION AND RECOVERY BY CHLORINATION

A. Apparatus and Method

For chlorination, the ore, in charges of from 30 to 40 grams, was spread out over about 18 inches of a 1-inch hard glass combustion tube. This tube was about 4 feet in length and was protected from breakage in the combustion furnace by a sheet of asbestos paper. (See Plate II.)

A slow current of chlorine, dried by passing thru D, a flask containing concentrated sulfuric acid, was led in a slow stream over the heated ore. The vapors of sulfur monochloride (S_2Cl_2) were collected in the side-necked flask B after passing thru the condenser A. A piece of rubber tubing on B made it possible to regulate the stream of chlorine, and to carry off the excess to the draft. The chlorinations were continued from 3 to 5 hours. In experiment #2, chlorination probably was not complete, since a small portion of the ore was in an unheated portion of the tube. This made it necessary to rechlorinate the residue from the hydrochloric acid extraction, but rechlorination failed to give the same results as on the original ore.

After the tube had cooled, it was taken from the furnace and as much residue as possible was removed directly

to a large casserole. The tube was partly filled with warm, very dilute hydrochloric acid and carefully shaken until all the residue on the sides of the tube was removed. The washings and rinsings of the tube were added to the residue in the casserole and the whole heated to boiling. After filtering and washing carefully with small portions of very dilute hot hydrochloric acid and boiling water, the residues were ignited and weighed. These residues had an entirely different appearance from the tailings secured in Part II by other methods----those obviously contained other constituents than silica; these all appeared to contain nothing but silica. The filtrates were heated to boiling and 1 cc. of a 10% barium chloride solution and 2 cc. of sulfuric acid solution were added. Three or four days after precipitation the crude sulfates were filtered off, dried and tested for activity, first by the film method, later by a quantitative assay. After the radium-barium sulfate had been separated, the solution remaining from chlorination #2 was diluted to 500 cc. ^{The emanation from} ~~200 cc.~~ ^{the solution} was boiled off and then stored in a tightly stoppered flask for a quantitative determination. (1)

(1) 200 cc. were also taken for an iron determination. 18.477 grams of Fe_2O_3 , corresponding to 27.765 grams of FeS_2 were obtained from 32.765 grams of original ore, i.e. the FeS_2 is 84.74% of the ore. This compares favorably with the figure 87.5% calculated from the amount of material not soluble in H_2SO_4 . See page 3.

B. Examination of Products

1. Physical Examination

	(2)			
Number of Experiment---	1-----	2-----	3-----	4(Carnotite)
Weight of ore-----	32.765g.--	36.158g---	30.852g.-----	13.332g.
Time chlorinated-----	4 $\frac{3}{4}$ hr.---	3 hr.-----	3-4 hr.-----	3 hr.
Weight of tailings----	3.166g.--	7.39g.---	3.389g.-----	11.198g.
Per cent of tailings--	9.66%	22.5%	10.98%	84%

Later when an assay for radium was made on the original ore, the ore being thoroughly oxidized with nitric acid, a residue of .1432 grams was obtained from 1.0205 grams of the original ore or 14.03%. This is larger than that obtained in either chlorination #1 or #3.

2. The Assays for Radium

After chlorination and recovery of the radium as radium-barium sulfates, the radium losses consist of the radium (1) remaining in the tailings and (2) that remaining in the solution from which the radium-barium sulfates have been separated by filtration. Also, in order to ascertain the percentage recovery of radium, it is necessary to know the radium content of the ore. The distribution of radium

(2) Since chlorination of #2 was not quite complete, this result should not be compared with #1 and #3.

among the above products was determined by the emanation method, following the particular procedure and precautions given by Lind. ⁽³⁾ Of the two electroscopes used, Lind #1 had a constant of 9.97×10^{-9} curies; Lind #2 had a constant of 8.47×10^{-9} curies, ⁽⁴⁾ i.e. a discharge of one division of the scale per second is produced by these quantities of radium emanation at the time of maximum activity -----three hours after the introduction of the emanation into the instrument.

The following radium determinations were made:

#1 and #2. The original ore for radium content.
 Samples of about 1 gram were weighed into a flask and the emanation boiled off with 1:1 nitric acid. In making this determination, it was found that the oxidation of the FeS_2 by the nitric acid resulted in the formation of nitric oxide, which is largely insoluble in sodium hydroxide, as well as nitrogen tetroxide. The volume of the gas thus obtained exceeded the capacity of the burette used for collecting the gases that contain the minute traces of emanation liberated. To obviate this difficulty, a small stream of oxygen was introduced directly into the chamber where the emanation was being collected, whereupon the nitric oxide was oxidized to the readily absorbable nitrogen dioxide.

#3 and #4. The original ore for emanation power.
 Samples of about 5 grams were sealed in a glass tube and stored for a definite period. The accumulated emanation was determined by drawing a stream of air thru the tube into an exhausted electroscope. The Operation was conducted at room temperatures.

(3) S.C. Lind, Practical Methods for the Determination of Radium. I. Interchangeable Electroscope and its Use. Jour. Ind. and Eng. Chem. Vol. 7. No. 5. p. 406. May 1915. Also Ibid, II. The Emanation Method. Jour. Ind. Eng. Chem. Vol. 7. No. 12. p. 1024. Dec. 1915.

(4) These were the electroscopes used by T.H. Leaming, Herman Schlundt and J. Underwood in their experiments on the "Comparison of the Ionization Currents Due to Equal Quantities of Radium Emanation in Different Types of Electroscopes." Trans. Am. electrochemical Soc. Vol. XXX, 1916. p. 375.

#5, #6, #7, #8, Crude Sulfates. Small samples (about .02g) were fused with mixed carbonates in a platinum boat, which was then stored in a sealed tube for a definite period and finally decomposed by 1:1 HNO_3 .

#9. Tailings. About one-half the amount left from chlorination of a 30-gram sample of the original ore (1.6g) in experiment #3 ~~was~~ fused with mixed carbonates, sealed off and decomposed by 1:1 HNO_3 .

#10. Solution from which crude sulfate was removed. 200 cc. of the 500 cc. filtrate were boiled off, sealed up and boiled off again after a storage period of several days.

No assay was made of the S_2Cl_2 . By the film method, the S_2Cl_2 left from #3 had no activity whatever.

In computing the amount of radium in a sample which had been stored for a definite time, t ,----a few days----, the fraction of emanation that accumulates during the time t , $(1-e^{-\lambda t})$, was taken from Appendix C of Rutherford's "Radioactive Substances and Their Radiations." (1913)

The percentage of radium in a given sample was calculated according to the formula, $\frac{K(R-L)T}{(1-e^{-\lambda t})W}$, where

- K = constant of electroscope
 R = maximum discharge of electroscope----divisions per second.
 L = natural leak of electroscope---divisions per second.
 T = weight obtained from original sample chlorinated.
 W = weight taken for the particular determination
 $1-e^{-\lambda t}$ = fraction of equilibrium amount of emanation formed in t days.
 λ = radioactive constant of radium emanation----
 ----.0.18day⁻¹.

The calculation of the radium present in the crude sulfate obtained from chlorination #1 (see below) illustrates how this formula is applied: The electroscope used was Lind #1; its constant, K , is 9.97×10^{-9} curies. The electroscope was discharged at the rate of 0.866 dps (R). The natural leak of the instrument, L , was 0.0084 dps. The effective

leak, R-L, was, then, 0.8576 dps. This sample was stored 4 days, 18 hours (t). The fraction of equilibrium amount of emanation formed in that time is found by reference to Rutherford's Appendix C---.5747. Substituting these values in the formula given above, we find that the amount of radium in the 0.0273 gram of crude sulfate is $\frac{(9.97 \times 10^{-9}) \cdot 8576}{.5747}$. The amount of radium in the whole sample taken for chlorination is obtained by multiplying by the factor $\frac{T}{W} \cdot \frac{.1621}{.0273}$, i.e. the ratio between the total sulfate weight and the weight of sulfate taken for the assay. The figure thus obtained is 8.838×10^{-8} grams of radium.

Complete data for the assays are given below:

Number of Experiment	1	2	3
Weight of original ore-----	32.765g.	36.158g.	30.852g.
Weight of tailings-----	3.166g.	7.388g.	3.389g.
Weight of sulfates-----	.1621g		0.0904g
Vol. of sol'n from above---	500cc-----	500cc.	500cc.

Assay of tailings(#1)

Weight (W)-----	1.5700g.
Storage Period (t)-----	4d, 16 hrs.
Electroscope used-----	Lind #2
Electroscope Reading (R)-	.0775 dps.
Electroscope Leak (L)---	.0135 dps.
Total Radium-----	1.954×10^{-9}

Assay of solution (#2)

Volume of solution-----	200cc.
Storage Period (t)-----	7 d., 23 hrs.
Electroscope Used-----	Lind #2.
Electroscope Reading (R)-----	.0380dps.
Electroscope Leak (L)-----	.0138dps.
Total Radium-----	4.23×10^{-10}

Number of Experiment	1	2	3
----------------------	---	---	---

Assay of sulfates

(a) Weight--(W)-----	.0273	-----	.0173
Storage Period (t)-----	4 d., 18hrs.	-----	3 d., 16hrs.
Electroscope Used-----	Lind #1	-----	Lind #2.
Electroscope Reading(R)---	.8660dps.	-----	1.0923dps.
Electroscope Leak(L)-----	.0084dps.	-----	.0146dps.
Total Radium-----	8.838×10^{-8}	-----	9.930×10^{-8}
(b) Weight (W)-----	.0275g.	-----	.0206g.
Storage Period (t)-----	4d., 20hrs.	-----	2 d., 18hrs.
Electroscope Used-----	Lind #2	-----	Lind #1.
Electroscope Reading(R)---	.9709dps	-----	.8814dps.
Electroscope Leak (L)---	.0125 dps.	-----	.0108dps.
Total Radium-----	8.229×10^{-8}	-----	9.757×10^{-8}

Assay of Original Ore---Radium Content

Sample-----	1	-----	2
Weight-----	0.9953g	-----	1.0205g
Electroscope Used-----	Lind #2	-----	Lind #1.
Electroscope Reading-----	.3673 dps.	-----	.3341 dps.
Electroscope Leak-----	.0133 dps	-----	.0238 dps.
Total Radium 2-----	2.999×10^{-9}	-----	3.094×10^{-9}
Total Radium per gram-----	3.013×10^{-9}	-----	3.031×10^{-9}

Assay of Original Ore---Emanating Power

Sample-----	1	-----	2
Weight-----	5.005 g.	-----	5.02 g.
Storage Period (t)-----	6 d., 23 hrs.	-----	8 d., 17 hrs.
Electroscope Used-----	Lind #2.	-----	Lind #2
Electroscope Reading (R)---	.1852 dps.	-----	.2062 dps.
Electroscope Leak (L)-----	.0128 dps.	-----	.0117 dps.
Total Radium-----	2.045×10^{-9}	-----	2.081×10^{-9}
Total Radium per gram-----	4.086×10^{-10}	-----	4.145×10^{-10}

By the film method, the tailings from chlorination #1 were found to have an activity of .0435 dps., i.e. the percentage of radium present in them would be 3.57%. This result for the radium present in the tailings is probably

more nearly correct than that obtained in the assay (1.74%), since it was very difficult to fuse the tailings with the mixed carbonates, and since decomposition by nitric acid was accordingly also difficult. Also the Emanation method is not so accurate where only small percentages of radium are present.

Altho an assay was made of the sulfates from chlorination #1, the values so obtained should be discarded in making an evaluation of the method, since these sulfates were precipitated and filtered off some three or four weeks before they were ignited and weighed and, moreover, this sample was not handled with as much care as the sulfates obtained from experiment #3. The sulfates from chlorination #3 were carried thru all the operations without mishaps, except that a very small particle of the second sample was lost thru cracking of the tube it was sealed into; accordingly in the average the first sample was valued three points and the second sample one point.

3. The Balance Sheet

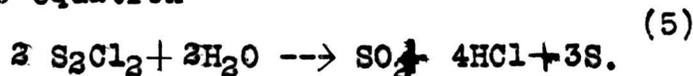
Number of Experiment	1	2	3
1. Description of Ore	80 mesh	80-mesh	80-mesh
2. Weight of Ore Used	32.765 g.	36.158g.	30.852g.
3. Weight of Tailings	3.166g. 9.66%	7.388 g. 22.5%	3.389g. 10.98%

Number of Experiment-----	1-----	2-----	3-----
4. Length of chlorination---	4 hr;45min-----	3hr-----	3-4hr.
5. Volume of solution-----	350cc-----	400cc-----	350cc.
6. 10% Barium Chloride Added	1cc-----	1cc-----	1cc.
7. Total Radium:in ore-----	1.125×10^{-7} -----	1.241×10^{-7} -----	1.059×10^{-7} -----
8. Total Radium:in sulfates-----	-----	(a) 9.930×10^{-8} -----	-----
	-----	(b) 9.757×10^{-8} -----	-----
	-----	average 9.887×10^{-8} -----	-----
8a. Recovery of Radium as sulfates-----	-----	(a) 93.75%-----	-----
	-----	(b) 92.1%-----	-----
	-----	average 93.34%-----	-----
9. Total Radium;intailings--	1.954×10^{-9} -----		
(Emanation method)	1.74%-----		
10. Total Radium: in tailings	3.57%-----		
(Film method)			
11. Total Radium: in liquors-----	-----	4.23×10^{-10} -----	-----
	-----	0.341%-----	-----
12. Radium per gram:of ore---	3.433×10^{-9} -----	3.433×10^{-9} -----	3.433×10^{-9} -----
13. Radium per g.of sulfates-----	-----	(a) 1.0982×10^{-6} -----	-----
	-----	(b) 1.0791×10^{-6} -----	-----
	-----	average 1.0934×10^{-6} -----	-----
14. Concentration Ratio-----	-----	(a) 318.5:1-----	-----
	-----	(b) 314.3:1-----	-----
	-----	average 317.5:1-----	-----
Radium in sulfates---	(Emanation method)-----	93.34%-----	93.34%-----
Radium in tailings---	(Emanation method)-----	11.74%-----	
Radium in tailings---	(Film method)-----		3.57%-----
Radium in solution---	(Emanation method)-----	0.34%-----	0.34%-----
		<u>95.42%</u> -----	<u>97.25%</u> -----
Radium unaccounted for-----	-----	4.58%-----	2.75%-----

In order to state positively that chlorination is an efficient method of extracting radium from pitchblendes,

it is necessary to extend the above experiments over a wider range of samples. However, the results described in this thesis point to a favorable extraction of higher grades of ore. The one trial on a carnotite indicates that this type of ore is not readily chlorinated, but further work on other samples may lead to more promising results.

No work has been done toward determining the possibility of commercial application of the method. The fact that the process is so simple----merely the passing of chlorine over heated ore, whereby the sulfur is converted to volatile S_2Cl_2 which is automatically removed by the heat, and whereby the iron and about 95% of the radium are converted to readily soluble chlorides-----suggests the feasibility of development on a large scale. The main points for consideration are: (1) the finding of a suitable material for the chlorination chamber; (2) the expense of providing chlorine and heat; (3) the utilization of by-products. Sulfur monochloride with water breaks down according to the equation



Recovery and utilization of each of these products would not appear to be an expensive process. Since the FeS_2 content was shown to be 85% or more of the ore, while the unattacked residue was about 10%, the problem of purifying the $FeCl_3$ in solution for commercial use should not be very difficult. But whether or not commercial use can be made of the method

(5) Alex. Smith, Gen'l Chem. for Colleges. p.267.

for low-grade pitchblendes, the possibility still remains of applying it to the extraction of radium from higher grade ores. The commercial development will also depend upon the supplies of pitchblendes of the kind studied,---an ore with a relatively high percentage of iron pyrites.

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APPENDIX

The experiments, described in this thesis, have been continued by Dr. Schlundt on higher grades of ore. His results on both medium and high grade ore indicate that the chlorination method applies equally well to the better grades of ore. Below is given a summary of results obtained in both sets of experiments:

Summary of Results

Grade of ore-----	Low-----	Medium-----	High
Weight of ore used--(a)	32.765g----	35.0g.-----	35.0g.
--(b)	30.852g----	35.0g.-----	35.0g.
Weight of tailings--(a)	3.166g----	1.24g.-----	3.46g.
	9.66% ----	3.54% -----	9.9%
--(b)	3.389g-----		3.60g.
	-10.98%-----		10.3%
Radium per g. of ore--	3.433×10^{-9} g-	8.312×10^{-9} g.-	49.27×10^{-9} g.
Uranium equivalent ex- presses as U_3O_8 .-----	1.20%-----	2.92%-----	17.45%
Total Radium in ore--(a)	1.125×10^{-7} --	2.909×10^{-7} g.-	17.245×10^{-7} g.
	--(b) 1.059×10^{-7} --	2.909×10^{-7} g.-	17.245×10^{-7} g.
Radium recovered in sulfates-----	(b) 9.93×10^{-8} ---	2.671×10^{-7} g.-	16.15×10^{-7} g.
Percentage radium in sulfates-----	(b) 93.34%-----	91.78%-----	93.68%
Radium losses:			
(a) In tailings---	1.954×10^{-9} --	4.36×10^{-9} ---	5.66×10^{-8}
(emanation method)			
Per cent in tails-	1.74%-----	1.53%-----	3.29%
(a) In tailings-----	3.57%-----	-----	-----
(Film Method)			

Grade of ore-----Low-----Medium-----High

Radium Losses:

(b) In solutions-- 4.23×10^{-10} --- 1.49×10^{-9} ---- 4.43×10^{-9} g.
 per cent in
 solutions-----0.34%----- 0.51%-----0.26%

Radium unaccounted for 4.58%----- 6.38%-----2.67%

Weight of sulfates--(a) 0.1621g-----
 --(b) 0.0904g.---0.237g.-----0.635g.

Radium per gram of
 sulfates----- (b) 1084×10^{-9} g-- 1137×10^{-9} g--- 2543×10^{-9} g.

Concentration Ratio-(b) 318:1-----136:1-----51.6:1.

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Extraction and recovery
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