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MIM-475

CHEMISTRY - RADIATION AND RADIOCHEMISTRY

Contract Number AT-33-1-GEN-53

MOUND LABORATORY
Operated By
MONSANTO CHEMICAL COMPANY
MIAMISBURG, OHIO

Price \$ 0.60

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

REPORT

FOR

GENERAL RESEARCH

APRIL 1 - JUNE 26, 1950

(Radium Volume)

(Project 7QA-D, 71A)

CLASSIFICATION CANCELLED

DATE FEB 26 1957 *CE*

For The Atomic Energy Commission

H. R. Canale

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Date: July 31, 1950

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SUMMARY

The development of a process for the separation and purification of radium is the objective of the work reported in this volume. The starting material is the K-65 residue from the uranium extraction of pitchblende ore.

The approach has been to investigate the Curie method with its more recent improvements to obtain detailed operating conditions and to develop new and improved methods wherever possible. The objective, in part, has been achieved in that the basic features of the Curie process have been tested in the laboratory and considerable detailed information obtained. New steps have been introduced into the process which show potentialities for improved operation. The process has still to be outlined in the final form and the remaining experimental details completed. Once the complete process has been developed in a workable form, the research will be directed toward the simplification of the operations as time permits. Additional research of this type should be of considerable value since the flow sheet for the separation is complicated by the complex nature of the starting material.

A procedure was developed for the removal of silica from the K-65 residue because difficulties were encountered with the formation of sodium silicate in the sodium hydroxide extraction of lead. The procedure required a water leach of the residue (9) followed by a hydrogen fluoride treatment of a sulfuric acid slurry (13). In the meantime further research on the lead extraction step showed that under the proper conditions the lead could be extracted without the sodium silicate interfering with the subsequent filtration (15). While the water leach and fluorination steps had certain

desirable features, it is not felt that the resulting improvement warrants the addition of two more operations in the process.

The research on the sulfate-to-carbonate conversion (27) has been studied in considerable detail. However, the study of the reaction at elevated temperatures and pressures has been delayed because the autoclave for this work has not been received from the manufacturer.

The radium-barium separation has been investigated by the customary fractional crystallization of the bromides (45) and also by the fractional precipitation of carbonates and chromates (48). The carbonate precipitation method is much less desirable than the chromate method because of the high cost of the trichloroacetic acid used and because the radium tends to concentrate in the supernatant solution. The chromate method shows considerable promise of useful application. The radium-barium separation also has been studied by ion exchange methods (61). These methods appear most applicable to the final radium purification after the preliminary concentration steps.

The handling of liquid wastes from the radium process (77) has progressed favorably. No major difficulties are anticipated.

Research has been continued in an effort to obtain more suitable methods for the measurement of radium, especially at low concentrations (82).

The engineering work (101) has been concerned mainly with the design of a pilot plant area, the preparation of cost estimates, and preliminary engineering flow sheets based on the most up-to-date procedure.

Problem Title - Water Leach of K-65 Residues
Report By - J. G. Stites
Work Done By - J. G. Stites and A. W. Martin

INTRODUCTION

When the initial research was started on the K-65 residues, a hydrofluoric acid treatment in the presence of concentrated sulfuric acid was used to remove the silica as a first step. The fact that brown fumes of nitrogen dioxide were evolved from the mixture when sulfuric acid was added indicated the presence of nitrates in the K-65 residue. Since nitrates and nitric acid present additional corrosion problems, especially in the large scale handling of the residues, it was deemed advisable to remove the soluble constituents by a water extraction.¹

DETAILED REPORT

Results of preliminary experiments indicated that 7 to 10 per cent of the K-65 residue was water soluble. Thus, an extraction would not only remove the undesirable nitrates but would also reduce the bulk of the residues by an appreciable factor.

Several experiments have been run in an attempt to find the optimum conditions for the extraction. The procedure for water extraction entailed adding the K-65 with stirring to the requisite amount of water which has been heated to the desired temperature, maintaining the temperature and agitation for a period of five minutes, and then filtering while hot. The residue from the filtration was washed with generous portions of water

and then sucked as dry as possible on a Buchner funnel. The wet residue was then weighed, dried at 110° , and reweighed.

The filtrates were sent to the analytical group for analysis. An average analysis of the water soluble material shows 12 per cent NO_3^- , 52 per cent $\text{SO}_4^{=}$, and 1.5 per cent CO_2 .

Duplicate runs were made in which the hot water was added to the K-65 residue. In such cases, some caking was noticed, and there was not as much water soluble material extracted as when the residue was added to the water.

All of the results in Table I were obtained by adding K-65 to water. The data indicate that washing the residue thoroughly after leaching results in more complete removal of water soluble salts. There, also, is more complete removal of soluble salts if a ratio of at least one liter of water to one pound of K-65 residue is used.

No radium has been found in the water soluble fraction. Immediately after filtration there was some activity noted in the filtrate, but this activity rapidly decreased, indicating that radon (and/or daughters), and not radium, had dissolved in the water.

The optimum procedure found for the extraction is to add K-65 residue to boiling water (one pound per liter), to stir while maintaining the boiling, and finally to filter and wash immediately with 400 to 600 milliliters of water. Such a treatment removes virtually all of the nitrates from the K-65 residue.

During agitation at the boiling temperature, there is considerable frothing; the mixture approximately doubles in volume. The froth is easily

broken by cooling or by discontinuing the agitation. The mixture is easily filterable. Upon drying after filtration there is no evidence of caking.

REFERENCE

1. Quarterly Report for General Research, MLM-443-2, p. 2-4.

Table IDATA ON EXTRACTION OF K-65 RESIDUES

Exp. No.	Wt. of K-65 (grams)	Vol. of H ₂ O (ml.)	Temp. of H ₂ O (deg.)	Vol. Holdup (ml.)	Total Vol. Filtrate (ml.)	Solids In Filtrate (grams)	Water Extracted (per cent)
I	454	350	70	137	458	32.91	7.25
II	457.5	750	90	226	840	38.03	8.31
III	454	450	100	209	500	21.32	4.70
IV	460	1000	(Boiling) 100	231	1293	39.02	8.48
V	454	1000	100	241	1270	40.07	8.83
VI	454	1000	100	253	1350	41.00	9.00
VII	454	1000	100	231	850	37.45	8.25
VIII	454	1000	100	237	1250	39.50	8.70
IX	454	1000	100	251	1070	43.12	9.50
X	454	1000	100	242	1375	41.54	9.10

Problem Title - Fluorination of K-65 Residues
Report By - J. G. Stites
Work Done By - J. G. Stites and A. W. Martin

INTRODUCTION

The residue remaining after the extraction of uranium from pitch-blende contains approximately 50 per cent silica. This silica, as reported in previous quarterly reports,¹ interferes with the removal of other elements in the radium recovery process, especially the removal of lead by treatment of the residue with concentrated sodium hydroxide.

The removal of silica as a first step in the recovery process not only would eliminate the difficulty encountered with the lead separation, but also would reduce the handling problem by decreasing the bulk of the residues as much as 50 per cent. Hydrogen fluoride in the presence of sulfuric acid has been used to remove the silica.

DETAILED REPORT

For the removal of silica, three batches from the water leach (ca. 1200 g.) were combined and placed in a cast iron reactor. To this residue one liter of 75 per cent sulfuric acid was added with stirring. Anhydrous hydrogen fluoride was then bubbled into the mixture through a copper tube. The temperature of the mixture was approximately 80° throughout the reaction. Hydrogen fluoride was added until no fumes from silicon tetrafluoride were noticed when a dish of water was held over the reaction mixture. This rather qualitative method of determining

completeness of reaction was found convenient to use in a drybox, since there was no convenient way to determine quantitatively the amount of hydrogen fluoride used.

By this procedure as much as 75 per cent of the silica can be removed; however, under the conditions outlined above, no more than 75 per cent of the silica has been removed.

After fluorination the mixture was diluted with three liters of water, stirred, and then filtered. The mixture filtered rapidly. The residue from the filtration was repulped in two liters of water and then refiltered. The purpose of this step was to remove the excess acid, since the next treatment of the cake was a sodium hydroxide digestion.

The residue from the repulping step was sucked as dry as possible. There is approximately one gram of water in five grams of residue or a 20 per cent holdup.

It is not necessary to dry the residue in preparation for the subsequent treatment. If the residue from the water leach had not been dried, undoubtedly it would be possible to add 95 per cent sulfuric acid directly rather than adding the 75 per cent acid. With acid more concentrated than 75 per cent the reaction does not proceed as well, and with more dilute acid there is a more serious corrosion problem.

REFERENCE

1. Quarterly Report for General Research, MLM-405-3, p. 3-9.

Problem Title - Removal of Lead Occurring as Lead Sulfate in K-65
Residue by the Use of Sodium Hydroxide

Report By - M. Economides and A. W. Martin

Work Done By - M. Economides and A. W. Martin

INTRODUCTION

Analysis of K-65 residues showed the presence of approximately 16 per cent lead and 45 per cent silica. Lead sulfate will be converted to lead carbonate in the carbonation of a mixture of lead, barium, and radium sulfates, and lead sulfate reacts with sodium carbonate more readily than barium sulfate. Thus, it is necessary to remove the lead which is present as lead sulfate before carbonation of the barium and radium sulfates. Lead can be removed from a mixture of lead and barium sulfates with an excess of sodium hydroxide. The lead hydroxide is soluble in an excess of alkali hydroxide forming a plumbite.

The excess of alkali hydroxide necessary to remove most of the lead must be kept to a minimum because of the presence of a large amount of silica. Although silicon dioxide does not react with water, it dissolves in solutions of the alkalies to form silicates.

The presence of sodium silicate makes the mixture difficult to filter. Experiments were run to ascertain the optimum conditions for the formation of lead plumbite from lead sulfate and a minimum quantity of sodium hydroxide.

These experiments comprised (1) lead sulfate with varying amounts of sodium hydroxide at room temperature and at boiling temperature; (2) a mixture of lead sulfate and barium sulfate with varying amounts of sodium hydroxide using both room temperature and boiling temperature; (3) a mixture of lead sulfate, barium sulfate and silica with varying amounts of sodium hydroxide both at room temperature and at boiling temperature; and (4) K-65 residue with sodium hydroxide using information obtained in the experimental data of the first three of these experiments.

The following procedure was used in determining the optimum conditions for the solubility of lead sulfate in sodium hydroxide:

Ten-gram samples of lead sulfate were weighed out. To the lead sulfate was added varying amounts of sodium hydroxide. In one series ten per cent sodium hydroxide was used, and in a second series fifteen per cent sodium hydroxide was used. The mixtures of lead sulfate and sodium hydroxide were stirred for fifteen minutes, then filtered through a weighed Gooch crucible. In one series the lead sulfate-sodium hydroxide mixture was stirred for fifteen minutes at room temperature. In a second series fifteen minutes at boiling temperature was used. The residue remaining on the Gooch crucible was washed, dried, and weighed. The filtrate was neutralized with sulfuric acid, and the lead contained in the filtrate precipitated as lead sulfate. Lead sulfate was collected as a residue on a weighed Gooch crucible. After drying and weighing, the amount of lead sulfate which had reacted with sodium hydroxide and had dissolved in solution as plumbite was determined. Results are summarized in Table I and Figures 1 and 2.

From these data on the extraction of lead sulfate with sodium hydroxide, it was concluded that approximately 200 milliliters of 10 per cent sodium hydroxide extracts lead as soluble lead plumbite from ten grams of lead sulfate at boiling temperature. Under the same conditions approximately 100 milliliters of 15 per cent sodium hydroxide is needed to produce the same results.

A ten-gram mixture of 7.3 grams of lead sulfate and 2.7 grams of barium sulfate was treated with 100 milliliters of fifteen per cent sodium hydroxide. Conditions for this experiment were the same as in the experiment on lead sulfate: boiling temperature for fifteen minutes. Lead is extracted to the extent of 98 per cent; however no barium appeared in the filtrate. No barium sulfate is extracted by sodium hydroxide under the conditions of these experiments.

From the information obtained on the extraction of lead from lead sulfate by sodium hydroxide, an investigation of the removal of lead from K-65 residue using sodium hydroxide was made. To obtain a filterable precipitate, one in which sodium silicate did not interfere, the quantity of excess sodium hydroxide was kept to a minimum. From the information obtained it appears likely that it will be possible to treat the original K-65 residue with sodium hydroxide.

The procedure for treating the K-65 residue with sodium hydroxide follows.

A 100-gram sample of K-65 was weighed out and placed in an 800-milliliter beaker. Fifteen per cent sodium hydroxide (127 milliliters) was added to the dry sample. The mixture was stirred continuously during

heating to boiling and while boiling. Boiling of the mixture was continued for one hour. The volume was kept approximately constant during heating by the addition of water. The mixture was filtered hot through a Buchner funnel, washed with 60 milliliters of hot, 15 per cent sodium hydroxide and finally with two 50-milliliter portions of hot water.

This same procedure was used on a 100-gram sample of K-65 substituting a 10 per cent solution of sodium hydroxide (253 milliliters) for the 15 per cent sodium hydroxide. The residue was washed with 100 milliliters of 10 per cent, hot sodium hydroxide and followed by two 50-milliliter portions of hot water.

Experimental results on the sodium hydroxide treatment of the K-65 residues are tabulated in Table II. Samples for chemical analysis of both the residue and the filtrate were given to Group 52. The analyses of these samples are incomplete. Table III represents data from reported chemical analysis of the residue of sample number one and extraction made using fifteen per cent sodium hydroxide.

Fifteen per cent sodium hydroxide removes approximately 30 per cent of the solids from the K-65 residue. Ten per cent sodium hydroxide removes approximately 40 per cent of the solids. Because of the incomplete removal of lead from the residues in one treatment with sodium hydroxide, a second treatment with sodium hydroxide using the same conditions is proposed.

Table ILEAD SULFATE WITH SODIUM HYDROXIDE

<u>10 Per Cent NaOH (ml.)</u>	<u>PbSO₄ in Filtrate Room Temperature (per cent)</u>	<u>PbSO₄ in Filtrate Boiling Temperature (per cent)</u>
53	30	41
106	35	77
212	45	99
 15 Per Cent NaOH (ml.)		
35	30	42
42.5	38	52
70	43	78
105	46	99
140	43	99
210	55	99

Table II100-GRAM SAMPLE OF K-65 RESIDUE

<u>Sample Number</u>	<u>NaOH Weight Per Cent</u>	<u>NaOH (ml.)</u>	<u>Weight Wet Residue (grams)</u>	<u>Weight Dry Residue (grams)</u>	<u>Filtrate (ml.)</u>
1	15	127	93.9	71.0	205
2	15	127	107.0	71.3	240
3	15	127	98.4	66.7	222
4	10	253	90.5	58.5	270
5	10	253	92.5	63.0	268
6	10	253	97.8	67.3	262
7	10	253	98.0	59.0	280
8	10	253	87.3	58.5	330
9	10	253	92.5	58.5	293
10	10	253	94.0	59.5	296

Table IIIPARTIAL ANALYSIS AT RESIDUES

<u>Sample Number</u>	<u>Constituent Sought</u>	<u>Found (per cent)</u>	<u>Weight Removed by NaOH From 100-Gram Sample (grams)</u>
1	SiO ₂	54.5	6.8
	Pb	4.32	13.2
	Ba	7.14	None

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FIGURE 1

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SOLUBILITY OF LEAD SULFATE IN 10 PER CENT SODIUM HYDROXIDE.

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FIGURE 2

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SOLUBILITY OF LEAD SULFATE IN 15 PER CENT SODIUM HYDROXIDE.

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Problem Title - The Solubility of Lead Sulfate in Saturated Sodium Chloride Solution

Report By - J. G. Stites

Work Done By - M. Economides and J. G. Stites

INTRODUCTION

The Union Miniere du Haut Katanga, one of the world's largest producers of radium, uses a saturated sodium chloride solution for the removal of lead from pitchblende residues. Inasmuch as sodium chloride is an inexpensive chemical, and, since it is desirable not to overlook any possible process which might be incorporated into the procedure for the recovery of radium from K-65, a preliminary investigation has been made to study the solubility of lead sulfate in saturated sodium chloride.

There is approximately 24 per cent lead sulfate in K-65. The removal of this lead must be achieved before attempting to carbonate the residues since lead is preferentially carbonated. Previous consideration has been given to the removal of lead by treating K-65 with sodium hydroxide. Treatment of K-65 with sodium hydroxide removes the lead as well as some of the silica. A sodium chloride treatment would not affect the silica in the K-65, and at this writing, it is not known how the increased silica content would affect the subsequent carbonation steps.

DETAILED REPORT

It has been found that one gram of lead sulfate is dissolved completely in a minimum of 30 milliliters of boiling sodium chloride solution saturated at 25°. Since saturated sodium chloride at 25°

contains 0.3855 grams of salt per milliliter, an 11.5 fold excess by weight of sodium chloride is required for complete solution of lead sulfate.

The reaction has been postulated as:

Parallel experiments were run using ammonium nitrate and ammonium chloride in place of sodium chloride. The lead sulfate is not appreciably soluble in ammonium nitrate. However a five-fold excess by weight of ammonium chloride dissolves the lead sulfate completely.

Upon dilution of the saturated sodium chloride solution there is an immediate precipitation of lead sulfate.

It can be seen that the regeneration of the brine can be attained merely by dilution and filtration. The solubility of lead sulfate decreases rapidly in more dilute sodium chloride solutions.

Experiments are now in progress on the removal of lead from K-65 by saturated sodium chloride solutions.

Problem Title - The Carbonation of K-65 Residues and the Recovery of Barium-Radium Concentrate

Report By - E. F. Joy

Work Done By - E. F. Joy

INTRODUCTION

Various methods for the recovery of radium from K-65 residues have been considered at this and other sites.¹ The initial work at Mound Laboratory led to consideration of a water leach of the K-65 residue followed by treatment with hydrofluoric-sulfuric acid to remove the bulk of the silica as the first steps in the process.² The next step proposed was the treatment of this low silica residue with sodium carbonate solution to convert barium and radium sulfates to carbonates. The carbonation step may be represented by the following equation:

The present study is concerned with this carbonation step and the subsequent recovery of the radium in a concentrate of barium sulfate that is free from lead.

In the early stages of the carbonation study it was found that the removal of lead before carbonation would effect a saving in the cost of the carbonation step. The study was therefore extended to include the removal of lead by treatment of the low silica residues with sodium hydroxide solution. A workable process was developed which was applicable to both low and intermediate silica content residues. The carbonation of the residues after lead removal was found to be easily effected with reasonable

amounts of sodium carbonate and to give a good recovery of radium. A further extension of the process to the direct treatment of K-65 residue was tried with promising results. It appears feasible to carry out a sodium hydroxide leach as the first step preliminary to carbonation and to eliminate the water leach and hydrofluoric-sulfuric acid treatments previously suggested.

Quantitative data have been obtained on the removal of lead and silica by sodium hydroxide treatment and on the carbonation and recovery of barium and radium from K-65 residues of varying silica content.

The conversion of barium sulfate to barium carbonate by treatment with sodium carbonate is an equilibrium reaction. The lower solubility of barium sulfate favors the formation of this salt and a reasonable conversion to the carbonate can only be obtained by using an excess of sodium carbonate. Virtually complete conversion can be obtained on a laboratory scale by fusion with a 10-fold excess of sodium carbonate. On a commercial scale this is not a practical procedure, and conversion is usually effected by treating with sodium carbonate solution under pressure. The conversion is not complete in one step but by filtering to remove sodium sulfate and repeating the carbonation, high conversions can be obtained. The reaction can also be carried out by boiling barium sulfate with sodium carbonate solution at atmospheric pressure, but the conversion is lower and the rate of reaction slower.

An experimental autoclave was ordered to study the carbonation of K-65 residues under pressure but has not arrived at this date. In the absence of a suitable autoclave, data were obtained on the reaction at atmospheric pressure with the idea that minimum conversions and reaction rates would be obtained which would serve as a guide until a more complete study could be made at higher pressures.

DETAILED REPORTCarbonation Studies on Pure Inactive Barium Sulfate

Data have been obtained on the carbonation of barium sulfate with 20 per cent sodium carbonate solution by heating to 95° to 100° with mechanical agitation. The time required for reaction was studied first using two moles of sodium carbonate per mole of barium sulfate. From Figure 1-A it is apparent that the carbonation reaction under these conditions reaches equilibrium after two hours and gives about 50 per cent conversion of the initial barium sulfate to barium carbonate. The subsequent carbonations were therefore carried out for a two-hour period at 95° to 100°.

Another series of experiments were performed to determine the relation between the excess of sodium carbonate used and the conversion of barium sulfate. The results are plotted in Figure 1-B. Essentially complete conversion can be obtained at a molar ratio of 15 to 20 for sodium carbonate and barium sulfate. By carrying out the carbonation in two steps, good conversions can be obtained with smaller amounts of sodium carbonate. For example, two carbonations with the same amount of sodium carbonate equivalent to four moles per mole of initial barium sulfate would give the following conversions.

First carbonation - molar ratio 4:1 - 71 per cent conversion. Twenty-nine per cent of the barium sulfate would remain unconverted.

Second carbonation - the same amount of sodium carbonate would now be $4 \times \frac{100}{29}$ or 13.8 moles per mole of remaining barium sulfate. From the graph this ratio would give 99 per cent conversion for this step leaving one per cent of the 29 per cent or 0.29 per cent of the initial barium sulfate unconverted.

[REDACTED] MEM-4

The overall conversion for the two steps would be 99.71 per cent. This can be compared with a single step carbonation for the same total amount of sodium carbonate, molar ratio 8:1, which would give only 91 per cent conversion.

Treatment of K-65 after Silica Removal

The treatment of K-65 residues from which varying amounts of silica had been removed by hydrofluoric acid was studied next. Three batches, each representing three pounds of K-65 residue were received after the preliminary steps of water leaching and treatment with hydrogen fluoride-sulfuric acid had been carried out. A summary of these batches is given in Table I.

A. Without Preliminary Lead Removal

Batch I was divided in three portions for separate treatment in Experiments 1, 2, and 3. The moist weight of each portion as well as the estimated equivalent weight of K-65 residue is given in Table II-A. In Experiment 1, 353 grams of the moist residue was carbonated with 225 grams of sodium carbonate under the same conditions used in establishing Figure 1-B. The sodium carbonate taken was based on five moles per mole barium sulfate plus an estimated amount for the lead present. The carbonated residue required 200 milliliters of concentrated hydrochloric acid to neutralize it. On filtering, crystals of lead chloride formed in the cooled filtrate. The filtrate was reheated, and lead and barium sulfates were precipitated.

Only seven grams of mixed sulfates were recovered of which 50 per cent was lead sulfate. The low recovery of barium from the first carbonation was due to the preferential formation of lead carbonate which is less soluble

[REDACTED]

than barium carbonate. On dissolving the carbonated residue in hydrochloric acid, the lead carbonate was converted to slightly soluble lead chloride which remained largely with the residue. At a later date, lead was removed from this residue by dissolving in hot, 15 per cent sodium hydroxide solution, and the barium-radium content was recovered by a second carbonation with 250 grams of sodium carbonate. In the absence of lead a recovery of 37.6 grams or 80 per cent of the barium sulfate was obtained in the second carbonation.

When lead is not removed first, the use of hydrochloric acid to dissolve the carbonated residue does not seem feasible since the bulk of the lead remains as lead chloride and must be converted to lead carbonate on the second carbonation before any appreciable amount of barium can be carbonated. To avoid this difficulty, nitric acid was used to dissolve the carbonates in Experiment 2. Two carbonations were carried out, filtering out the sodium sulfate formed in each case and washing with water. The final carbonated residue was dissolved in nitric acid and filtered. Mixed lead sulfate-barium sulfate (145.5 grams) was precipitated from the filtrate by adding a slight excess of dilute sulfuric acid. Lead sulfate was separated from the mixture by leaching with hot, 15 per cent sodium hydroxide solution. During the first treatment with 135 grams of sodium hydroxide, a part of the lead sulfate was converted to red lead oxide, but this redissolved on the second treatment with an additional 70 grams of sodium hydroxide. In this experiment 48.3 grams of barium sulfate or 100 per cent of that taken was recovered. By the above outlined process good recoveries

[REDACTED] MM-2

of barium and radium can be obtained without first removing lead but at the expense of a relatively high consumption of sodium carbonate.

B. With Preliminary Lead Removal

In Experiment 3, the removal of lead was carried out first by leaching the hydrofluoric-sulfuric acid treated residue with 15 per cent sodium hydroxide solution. Two carbonations were then made with five moles of sodium carbonate per mole of barium sulfate present. After each carbonation the carbonates were dissolved in hydrochloric acid. In the first step 78.5 per cent of the barium was carbonated and recovered, and nearly all of the remaining barium was recovered in the second carbonation. The final residue was analyzed spectroscopically and showed a trace of barium and 0.07 per cent lead. By first removing lead, good recovery of barium was obtained using less than half the sodium carbonate required in Experiment 2.

In Experiment 4, using treated K-65 residue from Batch II, the initial treatment with sodium hydroxide removed only 39 grams of lead sulfate. The reason became clear at the start of Experiment 5 (a second portion of Batch II) when it was found that 28 grams of sodium hydroxide was necessary to neutralize the residual sulfuric acid in the residue. As a result of the large amount of lead left in the residue in Experiment 4, the recovery of barium sulfate from the first and second carbonation was low. About 20 per cent of the radium was left in the residue as found by a gamma count. A third carbonation was therefore carried out, and an additional 10.4 grams of barium sulfate was recovered. The total value recorded as barium sulfate is high because of the presence of some lead sulfate.

[REDACTED]

The acid was taken into account in Experiment 5, and additional sodium hydroxide was added to complete the extraction of lead. As a result, 85 per cent of the lead sulfate was extracted. Nitric acid was used in dissolving the carbonated residues, and the recovery of barium sulfate was high. Radium was determined on the combined barium sulfate from Experiments 4 and 5 and indicated a 97 per cent recovery.

Experiment 6 was carried out on the treated residue from two pounds of K-65, largely for the purpose of recovering substantial amounts of purified barium-radium carbonate for use by others in the group on the barium-radium separation phase of the problem. The experiment was carried through rapidly and less care was taken in handling. The recoveries of barium and radium were low but were still 90 per cent or better.

At this stage, it was found that the presence of some lead and other impurities in the crude barium sulfate interfered with its use in the barium-radium separation studies. For this reason purification steps similar to those used in the Curie process were introduced. The crude barium sulfate concentrate was carbonated again by boiling with 20 per cent sodium carbonate solution. The resulting barium carbonate was dissolved in hydrochloric acid, and the solution was filtered. The excess acid was neutralized with ammonium hydroxide to pH 5, and hydrogen sulfide was introduced. The precipitated sulfides (largely lead sulfide) were filtered out, and the solution was treated with a small excess of ammonia to precipitate hydroxides. These were also filtered out, and barium and radium were recovered from the purified filtrate by precipitating with sodium carbonate solution. These two purification steps might be combined

and might also be effected by the use of barium hydroxide and barium sulfide as the precipitants as is done in the Port Hope process.

A spectroscopic analysis of the sulfide and hydroxide precipitates indicated that the principal constituent was lead. Traces of barium, magnesium, and iron were also found in the sulfide and a trace of magnesium and iron in the hydroxide precipitate. Both precipitates were radioactive, and the presence of polonium and bismuth isotopes with the sulfides and the presence of actinium with the hydroxides is suspected.

A sample of the purified barium-radium carbonate was also submitted for spectrographic analysis. The qualitative results were:

Strong	Ba
Moderate	-
Weak	Sr
Trace	Mg, Ca, Ti, Na, Pb

Semiquantitative results:

Sr	0.45%	Mg	0.0012%
Ca	0.20	Pb	0.01
Ti	0.0013	Na	0.2

Direct Treatment of K-65 Residue

In Experiment 7, the direct treatment of K-65 residue with sodium hydroxide solution was tried. A one-pound sample of K-65 was leached for one hour at 95° to 100° with a 15 per cent sodium hydroxide solution containing 200 grams of sodium hydroxide. The residue was filtered, washed, and retreated with an additional 100 grams of sodium hydroxide. Analysis of the sodium hydroxide filtrates showed that 39 per cent of the silica and 86 per cent of the lead sulfate were removed by this treatment. The

residue was carbonated twice in the usual manner with 100 grams of sodium carbonate, and the resulting carbonates dissolved in hydrochloric acid. The weights of residue after carbonation compare favorably with that for the hydrofluoric treated residues of Experiments 4 and 5 (Table II-C). The crude barium-radium sulfate was recovered from each carbonation, combined and recarbonated for purification as described under Experiment 6. The purified barium carbonate was analyzed for radium content. The indicated recoveries for barium and radium were 109 per cent and 107 per cent, respectively. These high recoveries were obtained in spite of the incomplete removal of lead in the first step of the process. No difficulty was experienced in filtration at any step except that a slightly longer filtration time was required for the first sodium hydroxide leach. In view of the good results obtained in this experiment, it appears feasible to treat K-65 residue directly with 15 per cent sodium hydroxide without preliminary removal of silica by hydrofluoric acid treatment.

The use of 15 per cent sodium hydroxide solution for the extraction of lead was based on the use of this concentration at Port Hope as reported by A. Kuebel.³ The use of solutions much over 5 normal or 16.8 per cent for dissolving lead sulfate results in the separation of yellow rhombic crystals of lead monoxide.⁴ The amount of sodium hydroxide required for dissolving a given amount of lead sulfate was not readily available from the literature. Data have been accumulated on this phase by M. Economides.⁵ In the presence of K-65 residue it was expected that larger amounts of sodium hydroxide would be required because of the presence of silica in varying amounts. In Experiment 3, low silica residue, it was found that

[REDACTED] MEM-37

1.82 grams of sodium hydroxide per gram of lead sulfate removed 82 per cent of the lead. In Experiment 5, intermediate silica residue, 2.21 grams per gram of lead sulfate removed 85 per cent of the lead. In Experiment 7, using a high silica residue, i.e., no preliminary hydrofluoric acid treatment, 2.87 grams per gram of lead sulfate removed 86 per cent of the lead.

The extraction of lead sulfate and silica by direct treatment of K-65 residue with 15 per cent sodium hydroxide was determined as a function of the excess of sodium hydroxide in a series of experiments summarized in Table III. From the table it can be seen that the extraction of silica reaches a maximum of about 41 per cent of the silica originally present. The lead sulfate extracted by 2.09 grams of sodium hydroxide per gram of lead sulfate is 82.0 per cent. The amount extracted increased only slightly with larger excesses of sodium hydroxide up to a maximum of 86.7 per cent. The total weight of residue to be carbonated is reduced by one half with a single leach of sodium hydroxide. Further study should be made of the sodium hydroxide treatment using a two-step leach and varying other conditions to find the best conditions for the extraction of lead with a minimum consumption of sodium hydroxide.

Radium Analysis

Radium analyses on recovered barium were made by the alpha slide technique. In the case of recovered barium carbonate, samples were dissolved directly in hydrochloric acid, bubbled overnight, and appropriate aliquots mounted on slides for counting. Barium sulfate samples were converted to the carbonate by fusing with sodium carbonate and extracting with water before dissolving in hydrochloric acid. The per cent recoveries

[REDACTED]

of radium given in Table II-B are based on a radium content of 335 micrograms of radium metal per pound of K-65 residue. This analysis of the K-65 has not been checked directly in this laboratory. However it corresponds closely with the value obtained by gamma count of an equilibrium sample compared with a radium standard.

From the above radium analysis and the analyzed barium content of the K-65 residue, the Ba:Ra ratio can be calculated as 76,900:1. The analyses of the purified barium carbonate recovered from K-65 in Experiments 1, 6, and 7 gave the following ratios:

Experiment No.	1	6	7
Ratio Ba:Ra	78,160	78,990	79,370

From these figures it can be concluded that the barium is effectively carrying the radium and that the final product will be a relatively rich concentrate containing 7.5 milligrams of radium per kilogram of barium sulfate.

REFERENCES

1. Babcock, A. B., Jr., Survey of Processes for Radium Recovery from Pitchblende Ores, Report NYO-112.
2. Martin, A. W., Quarterly Report for General Research, MLM-443-2, p. 4.
3. Kuebel, A., J. Chem. Ed. 17, 417-21 (1940).
4. Kohlschutter and Rosti, Ber. 56, 287 (1923).
5. Economides, M. and Martin, A. W., Quarterly Report for General Research, MLM-475, p. 15.

Table IHYDROGEN FLUORIDE-SULFURIC ACID TREATED K-65 RESIDUES USED
AS STARTING MATERIALS FOR RECOVERY OF BARIUM AND RADIUM

<u>Batch</u>	<u>K-65 Taken</u> <u>g.</u>	<u>Water Soluble</u> <u>g.</u>	<u>%</u>	<u>SiO₂ Removed</u> <u>g.</u>	<u>% of Total</u>	<u>Used for</u> <u>Experiment, No.</u>
I	1362	Not Deter.		435 ca.	70 ca.	1,2,3
II	1362	101	7.5	169	27.2	4,5
III	1362	136	10	322	51.9	6

Table II-A

RECOVERY OF BARIUM AND RADIUM. STARTING MATERIALS AND REAGENTS

Experiment	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
<u>Starting Material</u>							
K-65 Residue Treated with HF-H ₂ SO ₄ (g.)	353 ¹	339 ¹	258 ¹	365	365	600	-
Original K-65 Residue (g.)	486	497	379	454	454	908	454
SiO ₂ Taken (g.)	221	226	172	207	207	413	207
PbSO ₄ Taken (g.)	116	119	90.6	108	108	217	108
BaSO ₄ Taken (g.)	47.0	48.1	36.6	43.9	43.9	87.8	43.9
Ra (Micrograms)	359	367	279	335	335	670	335
<u>Reagents Used</u>							
1st Carbonation, Na ₂ CO ₃ (g.)	230	225	75	100	100	200	100
Acid (ml.)	200 ²	nd ^{3,6}	50 ²	nd ^{2,6}	28 ³	90 ³	nd ^{2,6}
2nd Carbonation, Na ₂ CO ₃ (g.)	250	225	75	50	100	200	100
Acid (ml.)	nd ⁶	nd ⁶	10	100	16	nd ⁶	nd ⁶
1st Leach for Pb, NaOH (g.)	150	135	135 ⁴	175 ⁴	175 ⁴	400 ⁴	200 ⁴
2nd Leach for Pb, NaOH (g.)		70			65	30	100
Purification of Crude BaSO ₄ :							
1st Carbonation, Na ₂ CO ₃ (g.)		174		136		345	110
2nd Carbonation, Na ₂ CO ₃ (g.)		9				345	18

Notes: 1. Weight of moist residue.
 2. Concentrated HCl.
 3. Concentrated HNO₃.
 4. NaOH treatment before carbonation.
 5. Na₂CO₃ was taken as a 20% aqueous solution and NaOH as a 15% solution in all experiments
 6. nd - not determined.

Table II-B

RECOVERY OF BARIUM AND RADIUM, REMOVAL OF LEAD

Expt.	PbSO ₄ -BaSO ₄ Recovered g.	PbSO ₄ Extracted g.	BaSO ₄ Recovered from Successive Carbonation				Purified BaSO ₄ g.	% of Taken	Ra Recovery	
			1st g.	2nd g.	3rd g.	Total g.			g. of Ra	% of Taken
1	7	nd*	3.5	37.6		41.1	}			
2	145.5	80.9		48.3**		48.3		95	950	95
3	-	74.2	28.3	7.6		35.9				
4	-	38.9	34.4	14.0	10.4	58.8		nd*	}	650 97
5	-	92.6	22.3	26.0		48.3		nd*		
6	-	nd*	133.4	23.4		156.8	81.6	93	606	90
7	-	93.4	35.8	19.2		55.0	47.9	109	360	107

*nd - not determined.

**BaSO₄ from 1st and 2nd carbonations combined.

Table II-C

RESIDUES AFTER CARBONATION AND ACID TREATMENT

<u>Expt.</u>	<u>Initial K-65 g.</u>	<u>After 1st Carbonation g.</u>	<u>Residue Weight</u>		<u>After 3rd Carbonation g.</u>	<u>% of K-65</u>	<u>Analysis of Final Residue</u>		
			<u>After 2nd Carbonation g.</u>	<u>% of K-65</u>			<u>SiO₂ %</u>	<u>PbSO₄ %</u>	<u>BaSO₄ %</u>
1	486	(309)	63	13.0					
2	497	nd*	99	19.9					
3	379	(80)	55	14.6			74.0	N11	N11
4	454	179	160	35.2	116.3	25.6	90.6	N11	N11
5	454	(171)	118	25.9			92.0	N11	0.96
6	908	247	209	23.1			81.5	N11	N11
7	454	165	141	31.1			**	**	**

Parentheses indicate weight of moist residue.

*nd - not determined.

**Analyses not complete.

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Table III

EXTRACTION OF SILICA AND LEAD FROM K-65 RESIDUE WITH 15 PER CENT
SODIUM HYDROXIDE - EFFECT OF VARYING THE EXCESS OF SODIUM HYDROXIDE

Expt.	Filtrate Analysis													
	K-65 g.	NaOH g.	H ₂ O g.	g. NaOH/ g. PbSO ₄	Pb		SiO ₂		PbSO ₄		Residue		Calculated Values	
					Extracted	% of	Extracted	% of	+ SiO ₂	% of	Dry Wt.	% of	Water	Total
					g.	Taken	g.	Taken	g.	Taken	g.	K-65	Soluble %	Accounted For %
1	50	25	142	2.09	9.8	82.0	9.0	39.6	18.8	37.6	25.7	51.4	8.8	97.8
2	50	37.5	213	3.14	10.22	85.5	9.34	41.0	19.56	39.12	25.5	51.0	8.8	98.9
3	50	50	283	4.19	10.03	84.3	9.33	41.1	19.36	38.72	25.2	50.4	8.8	97.9
4	50	62.5	354	5.23	10.36	86.7	9.15	40.3	19.51	39.02	25.0	50.0	8.8	97.8

Total accounted for is the sum of PbSO₄, SiO₂, insoluble residue and water soluble, calculated as % of K-65.

CONVERSION OF BARIUM SULFATE TO BARIUM CARBONATE.

CONDITIONS: BOILING AT ATMOSPHERIC PRESSURE,
20% SODIUM CARBONATE SOLUTION, MOLAR RATIO
OF SODIUM CARBONATE/BARIUM SULFATE = 2.

CONVERSION OF BARIUM SULFATE TO BARIUM CARBONATE,
EFFECT OF EXCESS SODIUM CARBONATE.

CONDITIONS: BOILING FOR TWO HOURS, ATMOSPHERIC PRESSURE,
20% SODIUM CARBONATE SOLUTION.

Problem Title - Fractional Crystallization
Report By - J. G. Stites
Work Done By - J. G. Stites and M. Economides

INTRODUCTION

Justification for further study on the separation of radium from barium by fractional crystallization lies in the facts that:

1. Fractionation of this kind has been used for the commercial production of radium.
2. There is disagreement in the literature on the effectiveness of separation by crystallization.
3. The use of fractional crystallization would not require the services of specialists for operation.

DETAILED REPORT

Data are incomplete at the present writing, but a summary follows of work which has been done.

The optimum solvent for the fractional crystallization of barium-radium bromides has been found to be 0.33 normal hydrobromic acid.¹ Accordingly, 86.15 grams of barium carbonate (60.0 grams barium) from K-65 was dissolved in a slight excess of 48 per cent hydrobromic acid. The solution was diluted and filtered. The carbonate was assayed for radium and found to contain 740 micrograms. This amount of radium represents a 81,000:1 barium to radium ratio.

The barium-radium bromide solution after filtration was evaporated until crystals formed when a stream of cool air was blown across the surface

of the liquid. The solution was then allowed to cool and crystallize. This was designated as Fraction I.

A schematic diagram of the fractionation is presented in Figure 1.

The partition factor, D, is calculated as:

$$D = \frac{\text{Ra:Ba (Crystals)}}{\text{Ra:Ba (Supernatant)}}$$

The partition factor as well as being influenced by the enrichment of radium is also greatly dependent on the total amount of salt crystallized. This factor explains at least in part the variation of the partition factor, D. The D values obtained agree with those reported by Hoskins and Doerner.²

Fractional crystallization, as a method of separating radium from barium, will be made the standard by which the other methods will be judged.

REFERENCES

1. Scholl, J. Am. Chem. Soc. 42, 889 (1920).
2. Doerner and Hoskins, J. Am. Chem. Soc. 49, 738 (1927).

Figure 1

A repeat of the above experiment gave the following results:

Problem Title - The Concentration of Radium from Barium Rich Mixtures
Report By - M. L. Salutsky
Work Done By - M. L. Salutsky

INTRODUCTION

Important criteria for the concentration of radium from barium-rich mixtures are time, separation, control, and cost. Two homogeneous phase reactions have been investigated for this purpose: the decomposition of trichloroacetate ions in hot solutions to precipitate insoluble carbonates, and the hydrolysis of urea in boiling solutions of alkaline earth dichromates to precipitate insoluble chromates.

The trichloroacetate method was reported and discussed in the previous quarterly report.¹ The method apparently depends upon the inability of barium carbonate to carry radium carbonate and upon a difference in solubility of the two carbonates. In agreement with the observations of Nikitin,² radium carbonate was found to be more soluble than barium carbonate.

The chromate-urea method depends upon the insolubility of radium chromate and the ability of barium chromate to carry radium chromate. The solubility of radium chromate has been estimated at 10^{-8} grams per liter.³ If this value is correct, then radium chromate is one of the most insoluble substances known. Fractional precipitation of barium-radium chromates yields precipitates enriched in radium. The acidity of the solution is controlled by the use of urea.

DETAILED REPORT

Analytical Methods

Radium was determined by the alpha counting technique of Tompkins and co-workers.⁴ Before applying this analytical procedure, the self-absorption of radium alpha particles by barium salts was determined. Synthetic mixtures of barium and radium chlorides were prepared, and solutions of these salts analyzed for radium. The recovery varied from 82 to 85.5 per cent (Table I). By carefully standardizing the procedure and applying the proper factor for absorption (usually 100/85), results within five per cent were obtained.

Barium was determined gravimetrically as the sulfate except when barium chromate was precipitated. In these cases barium chromate was weighed directly since barium chromate is anhydrous when dried at 110°.

In order to compare one enrichment step with another, partition factors were calculated.

$$D = \frac{Ra_p/Ba_p}{Ra_s/Ba_s}$$

D represents the partition factor, Ra_p the concentration of radium in the precipitate, Ba_p the concentration of barium in the precipitate, Ra_s , radium in solution, and Ba_s , barium in solution.

Trichloroacetate Method

One hundred grams of a barium-radium carbonate mixture purified from K-65 residues was taken as the original sample. The mixture contained 61.3 grams of barium and 794 microcuries of radium (Ba:Ra = 77,000:1).

The alkaline earth carbonates were dissolved in the calculated quantity of trichloroacetic acid. The resulting trichloroacetate solution was diluted with distilled water to a volume of about three liters. The solution was heated to 90° with an electric mantle. This temperature was maintained for one hour after the first appearance of a precipitate. During the heating the solution was stirred continuously. After cooling the mixture, the carbonate precipitate containing one-half to two-thirds of the total alkaline earths was filtered in a Buchner funnel and washed with a small quantity of water. The filtrate was reheated to 90° and the decomposition carried on for an additional hour. The mixture was cooled, and the precipitate filtered as before. In a similar fashion the filtrate was treated a third and fourth time to obtain a third and fourth carbonate fraction. To precipitate the remaining barium from the fourth filtrate, potassium trichloroacetate solution (prepared by dissolving 10 grams of potassium carbonate in the calculated quantity of trichloroacetic acid) was added and the solution of the mixed trichloroacetates heated. Potassium trichloroacetate hydrolyzes in hot solutions to produce potassium carbonate. Hence, the final solution was moderately alkaline ($\text{pH} > 8$). Without the addition of the potassium salt, it is difficult to precipitate all of the barium. This small quantity of barium carbonate was filtered and is designated as Fraction 5.

The five carbonate fractions were analyzed for barium and radium as described above. The results of these analyses along with the calculated Ba:Ra ratios are listed in Table II. It may be noted that better than 99.5 per cent of the barium was precipitated, although only about 75 per cent of

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the radium was carried with it. Less than 0.5 per cent of the original barium is associated in the final filtrate with 25 per cent of the original radium.

In order to account for the missing radium, the filtrate from Fraction 5 was evaporated to a small volume and the barium and radium recovered as sulfates. Analysis of this filtrate showed a ratio of 450:1 for the barium-radium content. However, a material balance for radium was not obtained because of some loss resulting from a laboratory accident.

The above experiment was repeated using Fraction 5 (Ba:Ra = 16,000:1) as the original sample. The procedure was the same as given above except that the total dilution was 500 milliliters, and only three barium carbonate fractions (Fractions 6, 7, and 8) were precipitated. The quantity of potassium trichloroacetic was reduced because of the smaller volume. One gram of potassium carbonate was dissolved in the minimum quantity of trichloroacetic acid, and this solution was added to the filtrate from Fraction 7.

The three carbonate fractions were analyzed for both barium and radium. The results of these analyses are listed in Table III. As before, approximately 99.5 per cent of the barium was precipitated in Fractions 6, 7, and 8, but only 75 per cent of the radium.

The filtrate from Fraction 8 was evaporated to a small volume, and the barium and radium were recovered as sulfates. An analysis of this sample (Ba:Ra = 466:1) proved that about 25 per cent of the original radium was actually in the filtrate from Fraction 8.

Partition factors (D) and reciprocal partition factors (1/D) were calculated to aid in the comparison of this method with other methods for separating radium and barium. These factors were calculated on the basis of the total carbonate precipitated.

Although the enrichment is large, the trichloroacetate method has several disadvantages. It is rather costly since large quantities of trichloroacetic acid would be required. The milligram quantities of radium-rich sample remain in a large volume of solvent, and recovery would be difficult. About 75 per cent of the radium is carried by the barium carbonate, and this necessitates the reworking of the entire barium sample a number of times to remove an economical quantity of the radium. However, the method may be profitable as a preliminary concentration step.

Chromate-Urea Method

The best partition factors reported for any barium-radium separation are obtained for the fractional precipitation of chromates.^{5,6} A comparison of the partition factors listed by Henderson and Kracek for various separations is made in Table IV. As a result the application of homogeneous phase reactions to the chromate separation was studied.

The original sample used in this study was an oven-dried barium-radium carbonate mixture purified from K-65 residues. The barium content was found to be 69.60 per cent and the Ba:Ra ratio 96,930:1.

About 7.4 grams of this carbonate, equivalent to five grams of barium, was dissolved in the minimum quantity of concentrated nitric acid, and the solution was diluted to 500 milliliters with 0.1 molar nitric acid. The nitrate solution was heated to 90°. The amount of potassium chromate

required to precipitate 20 per cent of the barium was dissolved in 50 milliliters of one molar nitric acid. This solution was added dropwise to the hot nitrate solution which was stirred continuously during the chromate addition. No precipitate was formed since barium chromate is soluble in hot, dilute nitric acid. About 15 grams of urea was added, and the solution was boiled and stirred. As the urea hydrolyzed, the acidity was reduced, and radium-enriched barium chromate precipitated. As a result of the rise in pH the mixture changed from an orange to a lemon-yellow color, thus acting as its own indicator. The reaction was continued until the solution reached a pH of 5-6. Since barium chromate is practically insoluble at this acidity, the liquid phase was colorless. Both phases were analyzed for barium and radium.

This experiment was repeated except that fractions of 35 and 50 per cent of the original barium were precipitated. As before, both liquid and solid phases were analyzed for barium and radium. The results of these analyses are listed in Table V.

The effect of concentration was studied by an additional experiment in which the concentration amounted to 27 grams of barium per liter of solution (Table VI). Three consecutive chromate fractions (Fractions 1, 2, and 3) were removed from this one sample which amounted to approximately 20, 16, and 13 per cent of the original barium, respectively. All three chromate samples and the final filtrate were analyzed for barium and radium. Calculations were made on the basis of the total chromate precipitated. For example, a 50 per cent sample was determined by adding the values of Fractions 1, 2, and 3. This method allowed three experiments to be run with a single sample.

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The agreement between the values of Tables V and VI indicates that if a certain percentage of barium is precipitated, it will carry a definite fraction of the radium present regardless of the original concentration. The fact that 50 per cent of the barium will carry 95 per cent of the radium appears from Table I to be a good working factor.

The chromate-urea method seems to satisfy the important criteria for concentrating radium, namely time, separation, control, and cost. The time involved per step is less than one hour, and the separation is excellent as proven by the partition factors obtained. The cost of the chemicals (nitric acid, urea, alkali chromate) is low in comparison to other methods.

Barium chromate is precipitated by boiling the urea solution containing the amount of chromate necessary to precipitate a definite fraction of the barium present. However, to rework a chromate precipitate by the same procedure, half of the chromate must be removed before treating with urea. The problem of removing half the chromate is under investigation. Either half the chromate will have to be reduced or half must be separated by precipitation with lead. Lead chromate was found to carry only a small amount of radium salts from a 0.3 molar nitric acid solution. The other alternative would require a time-controlled reaction during the hydrolysis of urea so that only half of the barium chromate precipitates. Such a timed reaction would introduce a problem in control.

REFERENCES

1. Salutsky, M. L. and Stites, J. G., Quarterly Report for General Research, MLM-443-2.

2. Nikitin, B. A., Trav. inst. etat radium (U.S.S.R.) 3, 228-37;
C.A. 31, 4590.
3. Kracek, F. C., "The Separation of Radium and Barium as Chromates,"
Ph.D. Thesis, University of Minnesota (1924).
4. Tompkins, P. C., Norris, W. P., Wish, L., and Finkle, R. D.,
"Methods for the Quantification of Radium" United States Atomic Energy
Document, MDDC-699 (1946).
5. Henderson, L. M. and Kracek, F. C., J. Am. Chem. Soc. 49, 738
(1927).
6. Hahn, O. and Strassman, F., Naturwissenschaften 27, 89 (1939).

Table ISELF-ABSORPTION OF RADIUM ALPHA PARTICLES BY BARIUM SALTS

<u>Ba:Ra Ratio</u>	<u>Microcuries of Radium per Milliliter of Solution</u>		<u>Recovery (%)</u>
	<u>Calculated</u>	<u>Found</u>	
336:1	36.0	30.8	85.5
1,740:1	14.4	12.3	85.4
17,400:1	1.44	1.22	84.7
174,000:1	0.144	0.118	82.0

Table IICONCENTRATION OF RADIUM BY THE TRICHLOROACETATE METHOD

<u>Sample</u>	<u>Ba (Grams)</u>	<u>Ra (Microcuries)</u>	<u>Ba:Ra Ratio</u>	<u>D</u>	<u>1/D</u>
Fraction 1	32.6	184	177,000:1	0.265	3.76
Fraction 2	16.0	98	164,000:1	0.144	6.95
Fraction 3	7.0	71	99,000:1	0.082	12.2
Fraction 4	2.3	38	60,000:1	0.057	17.5
Fraction 5	<u>3.3</u>	<u>199</u>	16,000:1	0.0047	212
Total	61.2	590	-	-	-
Original	61.3	794	77,000:1	-	-
Filtrate	-	-	450:1	-	-

Table III

CONCENTRATION OF RADIUM BY THE TRICHLOROACETATE METHOD

<u>Sample</u>	<u>Ba (Grams)</u>	<u>Ra (Microcuries)</u>	<u>Ba:Ra Ratios</u>	<u>D</u>	<u>1/D</u>
Fraction 6	2.15	37.0	58,000:1	0.123	8.12
Fraction 7	0.57	20.1	28,000:1	0.0844	11.9
Fraction 8	<u>0.57</u>	<u>95.5</u>	6,000:1	0.00281	356
Total	3.29	152.6	-	-	-
Original (F-5)	3.31	199	16,000:1	-	-
Filtrate	25.62×10^{-3}	55.0	466:1		

Table IV

COMPARISON OF FRACTIONAL METHODS FOR THE CONCENTRATION OF RADIUM

<u>Salt</u>	<u>Partition Factor (D)</u>
Chromates	15.5
Bromides	9.0
Chlorides	4.37
Sulfates	1.70

No Separation $D = 1$

Table V

CONCENTRATION OF RADIUM BY THE CHROMATE-UREA METHOD

<u>Per Cent Barium Precipitated</u>	<u>Per Cent Radium Carried</u>	<u>Ba:Ra Ratios</u>		<u>Partition Factor (D)</u>
		<u>Precipitate</u>	<u>Solution</u>	
20.9	67.9	32,000:1	257,000:1	8.0
35.8	88.6	39,900:1	554,000:1	14.0
52.4	94.3	53,600:1	799,000:1	15.0

Original Concentration = 10 grams barium per liter.

Original Ba:Ra Ratio = 96,000:1.

Table VI

CONCENTRATION OF RADIUM BY THE CHROMATE-UREA METHOD

<u>Fraction</u>	<u>Per Cent Barium Precipitated</u>	<u>Per Cent Radium Carried</u>	<u>Ba:Ra Ratios</u>		<u>Partition Factor (D)</u>
			<u>Precipitate</u>	<u>Solution</u>	
1	20.6	65.3	32,200:1	233,000:1	7.3
1 & 2	37.3	86.9	43,800:1	486,000:1	11.2
1 & 2 & 3	50.6	95.2	54,200:1	1,050,000:1	19.4

Original Concentration = 27 grams barium per liter.

Original Ba:Ra Ratio = 96,900:1.

FRACTIONATION OF Ra AND Ba BY PARTIAL
PRECIPITATION OF CHROMATES

Problem Title - The Separation of Radium and Barium by Ion Exchange
Report By - W. C. McCluggage
Work Done By - W. C. McCluggage and S. R. Barth

INTRODUCTION

The separation of the radium and barium from K-65 residues of the uranium extraction process is being attempted by ion exchange. This process lends itself to remote control more readily than does the fractional crystallization method. It is also expected that the ion exchange will effect an economy of space and production costs.

The separation of two metals by an ion exchange column depends upon the preference shown by the resin for one ion under a given set of conditions. This preference is influenced by at least six factors: (1) the type of resin and its available cation, i.e., sodium, hydrogen, barium, lead, etc., (2) the solution composition, (3) the acidity of the solution, (4) the ionic radii of the metal ion, (5) the charge of the metal ion, (6) the presence of complexing agents in the solution phase.

The barium-radium ratio of the concentrate from K-65 residue is expected to be 75,000:1. Two ion exchange techniques are applicable for the different stages of radium purification. The "break-through" method consists of passing the original solution through a column until the first trace of radium is detected. Before radium appears, pure barium solution has been discharged from the column, and an enrichment of the radium still contained by the column has occurred. Upon several repetitions of this process, the barium-radium ratio may be concentrated to a ratio of 1,000:1

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or less. The final barium-radium separation of the concentrated solution would then be accomplished by the elution technique or by use of another separation procedure as precipitation or crystallization methods.

Measuring distribution coefficients of barium and radium will establish composition, pH, resin form, and temperature for the barium-radium separation by ion exchange. Engineering studies would still be necessary to make the method workable for large quantities of radium.

Separation of barium and radium from a 30,000:1 mixture has been accomplished on a laboratory scale by Tompkins.¹

DETAILED REPORT

Equilibrium Studies

Equilibrium studies between barium chloride and the barium form of Dowex 50 resin have been made. These studies were repeated using barium nitrate and barium acetate.

One-gram samples of air dried, barium form, 40-mesh, Dowex 50 were placed in 13-by-100-millimeter test tubes. One milliliter of the barium chloride stock solution was added followed by one milliliter of the radium stock solution. The test tubes which had previously been constricted near the top were sealed and then tumbled overnight to effect equilibrium. One milliliter of the solution was withdrawn from the tube and analyzed for radium by a modification of a method described by P. Tompkins.^{2,3} Barium nitrate and barium acetate solutions were treated in the same manner. The results are shown in Table I and Figure 1.

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To minimize the analytical work, a barium form of resin containing 151,000 micrograms of barium per gram of resin is used. Standard barium solutions are used. The difference of the alpha count of the radium stock solution before and after equilibrium gives the amount of radium that has remained on the resin. The amount of barium that leaves the resin is small compared to the large concentrations involved; therefore, it is not considered.

Break-Through Method

To test the ability of a column to concentrate a mixture of radium and barium, a liter of solution containing 35 micrograms of radium bromide and one equivalent of barium chloride was fed into a column of sodium form Dowex 50. The column was 12 millimeters in diameter, and the bed depth was 75 centimeters. The resin weighed 58 grams. Its capacity for barium was approximately 14 per cent of the metal ion in the feed solution. The column retained 52 per cent of the initial radium. A concentration factor of four is thus obtained. The initial ratio for barium to radium was 1,962,000:1. The final ratio was 500,000:1. The data for this work is given in Table II and Figure 2.

Elution Method

The work of E. R. Tompkins¹ was on low concentrations of radium and barium. A separation has been made in which the barium content was 30 times greater than that used by Tompkins, and the radium content was 3.8 times greater.

The column for this separation was 3.46 square centimeters in cross section and contained a 62-centimeter bed of the sodium form, 70 to 100 mesh, Dowex 50 resin.

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The feed solution, one liter in volume, contained 57.5 micrograms of radium bromide and 1.7376 grams of barium chloride. It was weakly acidic. This solution was passed through the column at the rate of 0.5 ± 0.1 milliliter per square centimeter per minute. This slow drop rate permitted the metal ions to be held on a narrow band of resin at the top of the column.

The feed solution was followed by three column volumes (345 milliliter) of water. The barium elutrient solution (10 per cent ammonium citrate by weight at pH 4.9) was introduced at the rate of 0.3 ± 0.1 milliliter per square centimeter per minute. This drop rate proved to be too slow. A band of barium citrate precipitated near the top of the column. The drop rate was increased to about one milliliter per square centimeter per minute in order to dissolve the barium citrate. The first barium appeared in the 16th 100-milliliter fraction. The concentration in the effluent increased rapidly then fell gradually to zero in the 41st fraction. A slight trace of radium appeared in the 26th fraction but did not increase appreciably during the barium removal. The radium elutrient solution (15 per cent ammonium citrate by weight and 10 per cent concentrated ammonium hydroxide by volume, pH 10 freshly prepared) was added at the end of the 42nd fraction. The 43rd fraction contained the final column volume of the barium elutrient. The 44th, 45th, and 46th fractions contained 98 per cent of the initial radium. These data are summarized in Table III and Figure 4.

The material balance was satisfactory for this run. The barium return was 101 per cent, and the radium return was 102 per cent. These results are well within the margin of error inherent in the methods of analysis used.

[REDACTED]

The method used in the barium analysis will not detect barium in quantities less than 0.5 milligram per 100 milliliters of solution; therefore, the barium elution curve is extrapolated to zero as shown in Figure 4.

REFERENCES

1. Tompkins, E. R., Separation of Radium from Barium by the Use of an Ion-Exchange Column Procedure, AECD-1998.
2. Tompkins, P. et al., Methods for the Quantification of Radium, MDDC-699.
3. McCluggage, W. C., Radium Analysis Methods, MLM-475, p. 82.

Table I

THE DETERMINATION OF ALPHA FOR BARIUM ACETATE SOLUTIONS

Barium Normality	pH	c./min./ Sample	Ba(res) Micrograms	Ba(sol) Micrograms	Ra(res) Micrograms	Ra(sol) Micrograms	Alpha
1.00	4.2	2.24 x10 ⁵	149,700	137,360	0.946	0.204	4.26
0.50	4.0	1.20 x10 ⁵	149,700	68,680	1.045	0.105	4.56
0.25	1.9	0.640x10 ⁵	149,700	34,340	1.092	0.058	4.40
0.10	1.5	0.275x10 ⁵	149,700	13,736	1.125	0.025	4.15
0.05	1.1	0.113x10 ⁵	149,700	6,868	1.149	0.001	5.25
0.02	1.1	0.065x10 ⁵	149,700	2,747	1.145	0.005	4.21

THE DETERMINATION OF ALPHA FOR BARIUM NITRATE SOLUTIONS

Barium Normality	pH	c./min./ Sample	Ba(res) Micrograms	Ba(sol) Micrograms	Ra(res) Micrograms	Ra(sol) Micrograms	Alpha
0.30	1.6	1.030x10 ⁵	149,700	41,200	0.955	0.093	2.88
0.20	1.6	0.649x10 ⁵	149,700	27,470	0.989	0.059	3.04
0.05	1.7	0.347x10 ⁵	149,700	6,867	1.015	0.033	1.42
0.025	1.7	0.248x10 ⁵	149,700	3,430	1.022	0.026	0.99
0.01	1.7	0.149x10 ⁵	149 700	1,375	1.031	0.017	0.60

THE DETERMINATION OF ALPHA FOR BARIUM CHLORIDE SOLUTIONS

Barium Normality	pH	c./min./ Sample	Ba(res) Micrograms	Ba(sol) Micrograms	Ra(res) Micrograms	Ra(sol) Micrograms	Alpha
1.00	--*	1.900x10 ⁵	149,700	137,000	0.875	0.173	4.7
0.30	1.6	0.843x10 ⁵	149,700	41,100	0.973	0.077	3.5
0.10	1.6	0.413x10 ⁵	149,700	13,700	1.01	0.05	1.8
0.03	1.7	0.250x10 ⁵	149,700	4,110	1.02	0.03	0.94
0.015	1.7	0.212x10 ⁵	149,700	2,050	1.03	0.02	0.70

* pH was not taken.

The following symbols are used. Ba(res) = barium per gram of barium form resin. Ba(sol) = barium per two milliliters of solution. Ra(res) and Ra(sol) are defined in the same manner. Alpha is the ratio of the distribution coefficients of radium and barium between the solution and the resin. The distribution coefficient of Ra(D(Ra)) is given by the expression $D(Ra) = \frac{Ra(res)}{Ra(sol)}$. D(Ba) is obtained in the same way.

$$\text{Alpha} = \frac{Ra(res)}{Ra(sol)} \bigg/ \frac{Ba(res)}{Ba(sol)}$$

All concentrations are expressed as micrograms per sample.

Table II

DATA ON BREAK-THROUGH METHOD

<u>Feed Solution Fraction No. and Volume (milliliters)</u>	<u>Weight of Ba per Fraction (grams)</u>	<u>Per Cent of Total Ba</u>	<u>c./min./ Fraction (x 10⁵)</u>	<u>μg. Ra per Fraction</u>	<u>Per Cent of Total Ra</u>
1 - 105	0.0	0.0	0.0	0.0	0.0
2 - 85	0.0	0.0	0.0	0.0	0.0
3 - 100	2.66	3.9	7.80	0.605	1.73
4 - 51	2.24	7.1	7.24	0.655	3.60
5 - 51	2.70	11.1	7.35	0.665	5.50
6 - 55	3.46	16.1	10.43	0.943	8.20
7 - 60	5.61	24.2	14.73	1.335	12.0
8 - 55	4.04	30.2	12.95	1.172	15.4
9 - 55	4.81	37.2	15.73	1.425	19.4
10 - 55	5.15	44.7	15.50	1.405	23.4
11 - 50	4.38	51.0	15.50	1.405	27.4
12 - 52	3.82	56.6	16.82	1.522	31.8
13 - 52	3.28	61.5	18.10	1.635	36.4
14 - 110	8.47	73.6	16.30	1.475	40.7
15 - 110	7.48	84.7	17.10	1.550	45.0
16 - 73	0.02		11.80	1.070	48.2
17 - 200	0.0		0.80	0.072	
18 - 100	0.0		1.00	0.090	

Table III

BARIUM AND RADIUM ELUTION

<u>Fraction Number</u>	<u>Barium Content Per Volume</u>	<u>Per Cent of Total Barium</u>	<u>Radium Content in Micrograms</u>	<u>Per Cent of Total Radium</u>
1-16	0.0030 g.	0.17		
17	0.0893	5.15		
18	0.2265	13.1		
19	0.2060	11.9		
20	0.1925	11.1		
21	0.1650	9.50		
22	0.1442	8.32		
23	0.1170	6.75		
24	0.1340	7.72		
25	0.1050	6.05		
26	0.0858	4.95	0.011	0.02
27	0.0446	2.57	0.025	0.04
28	0.0460	2.65	0.036	0.06
29	0.0343	1.98	0.045	0.08
30	0.0378	2.18	0.058	0.10
31	0.0385	2.22	0.085	0.15
32	0.0261	1.50	0.109	0.19
33	0.0165	0.95	0.118	0.21
34	0.0113	0.65	0.121	0.21
35	0.0089	0.51	0.137	0.24
36	0.0098	0.56	0.137	0.24
37	0.0061	0.35	0.156	0.26
38	0.0049	0.28	0.156	0.27
39	0.0027	0.16	0.152	0.26
40	0.0012	0.07	0.172	0.30
41			0.233	0.41
42			0.298	0.52
43			0.430	0.75
44			18.4	32.0
45			36.5	63.0
46			1.65	2.87
47			0.023	0.04
48				
49				
50				

63

THE RATIO (α) OF THE DISTRIBUTION COEFFICIENTS OF RADIUM AND BARIUM IN ACIDIC CHLORIDE, NITRATE AND ACETATE MEDIA.

FIGURE 1

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RADIUM CONCENTRATION BY ION-EXCHANGE

FIGURE 2

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THE SEPARATION OF RADIUM AND BARIUM

EXTRAPOLATION OF THE BARIUM ELUTION CURVE

MLN-476

Problem Title - The Decontamination of Liquid Wastes from the Radium Process
Report By - R. W. Moshier
Work Done By - R. W. Moshier

INTRODUCTION

Waste disposal from any radiochemical process requires that anything disposed of to natural waters be sufficiently low in radioactivity to be harmless to plant and animal life. The problem of waste disposal from the radium recovery program consists of removal of radioactive elements and chemical poisons from the waste solutions of the processes, and concentrating them in as small a bulk as possible for burial.

From bench-scale processing of K-65 residue the average quantity of wastes has been determined as well as their radioactive contents.

Processes have been fairly well worked out for the decontamination of these wastes to a relatively low activity count: better than 99 per cent removal. Where possible, this decontamination makes use of precipitation-carrying of the activity utilizing elements already present in the wastes. When necessary this is supplemented with added chemicals.

DETAILED REPORT

The counting in this work was performed with the parallel-plate alpha counter of approximately 50 per cent geometry, and the Nuclear Measurement Corporation PC-1 windowless chamber counter with a 50 per cent geometry. Counts were made with 0.100 milliliter mounts on one-inch by three-fourths-inch glass slides with the sample covering an area of

approximately 1.5 by 1.25 centimeters. No corrections have been made for sample thickness. Also the identities of the radioactive elements have not been determined.

Better counting will be attempted using two-inch glass circles, thus lowering self-absorption and also permitting the mounting of larger samples.

The following average activities have been found in the liquid wastes from the bench-scale radium recovery work:

<u>Waste Solution</u>	<u>c./min./ml.</u> <u>Alpha</u>	<u>c./min./ml.</u> <u>Beta</u>
1. Water Leach	52	127
2. Hydrofluoric-Sulfuric Acid Filtrate	5,080	5,400
3. Sodium Hydroxide Leach	480	12,000
4. Carbonation Filtrate	190	3,900
5. Sulfate-Precipitation Filtrate	39,000	63,000

Water Leach Decontamination

1. Tannic acid precipitant: a precipitate forms but decontamination is poor.
2. Formation of ferrous ferrocyanide: poor decontamination.
3. Aluminum sulfate: aluminum hydroxide produced with addition of ammonium hydroxide gives poor decontamination.
4. Silica gel: passage through a column of silica gel gives poor decontamination.

5. Lead chloride: treatment with 200 parts per million of lead with formation of lead sulfate from the sulfate ion already present lowers both the alpha and beta count to one fourth the initial value.

6. Barium chloride: treatment with 40 to 400 parts per million of barium, with formation of barium sulfate from the sulfate ion already present, lowers both the alpha and beta count to background level. This is by far the simplest and most efficient method for decontamination of water leach waste solution.

Sodium Hydroxide Leach and Hydrofluoric-Sulfuric Acid Filtrate

1. Neutralizing sodium hydroxide leach with 50 per cent chemically pure sulfuric acid gives fair results, as follows:

<u>pH</u>	<u>Alpha c./min./ml.</u>	<u>Beta c./min./ml.</u>
7.0	0	260
7.5	0	285
8.0	0	275
8.5	0	300
9.0	10	190

2. Neutralizing sodium hydroxide leach with hydrofluoric-sulfuric acid filtrate yields better results at the higher pH. At an end point of pH 5 both the alpha and beta counts per minute per milliliter are about 300; and also filtration is rendered difficult to impossible because of gradual separation of gelatinous silica. At neutral points of pH 7.5 to 9.0 the final counts average alpha 50, beta 65 counts per minute per milliliter.

3. Best results are obtained by slowly neutralizing, with rapid stirring, subsequent stirring for at least one hour, letting stand overnight before filtering and having a final pH of 8 to 9. The count on the filtrate runs consistently alpha 40 to 50, beta 0 to 40 counts per minute per milliliter. Equally good results are obtained by neutralizing with chemically pure sulfuric acid using this procedure. Likewise sodium hydroxide leach waste solution, obtained as a first treatment of K-65 residue, can be neutralized with chemically pure sulfuric acid giving equally good results.

Mixing All Wastes in a Ratio Approximating their Yield from Bench-Scale Operation

1. Very good decontamination was obtained by this proportionate mixing of all wastes with precipitation. The order of mixing has an important bearing on the results. For best results one proceeds as follows: To 25 milliliters of sulfate-precipitation leach, 25 milliliters of water leach are added. This gives a white precipitate. Without filtering, 50 milliliters of carbonation filtrate are added. Now slowly, with rapid stirring, 23 milliliters of hydrofluoric-sulfuric acid filtrate are added. As neutrality is approached, carbon dioxide is evolved, and the rate of acid addition must be slowed down. Finally, at pH 2 all the carbonate has been destroyed. Next, 25 milliliters more of the acid are added. This mixture is now used to neutralize 100 milliliters of sodium hydroxide leach which is performed by the best method as described above under sodium hydroxide leach. The results are alpha 130 and beta 102 counts per minute per milliliter.

2. By mixing water leach, carbonate filtrate and sodium hydroxide leach and then bringing to pH 7 with hydrofluoric-sulfuric acid filtrate decontamination is poorer, namely alpha 365, beta 425 counts per minute per milliliter. If the acidity is brought up to only pH 9 no foaming trouble is encountered and the decontamination is better; i.e., alpha 170 and beta 390 counts per minute per milliliter.

3. Further decontamination of the filtrates from these solutions by small additions of barium or lead ion lowers the alpha activity somewhat but has no effect on the beta activity.

4. The wet filter cake obtained from all experiments where sodium hydroxide leach is involved weighs approximately 0.2 grams per milliliter of solutions used. This cake evolves 70 per cent moisture at 110°.

Summary

1. Water leach waste decontamination process lowers the activity count to background level.

2. Sodium hydroxide leach waste decontamination process lowers the activity count to alpha 45 and beta 0 to 40 counts per minute per milliliter.

3. Hydrofluoric-sulfuric acid filtrate when used in the process for 2 gives the same low decontamination activity count.

4. When all wastes in the proportion obtained in bench-scale work are mixed, a decontamination process lowers the activity count to alpha 130 and beta 102 counts per minute per milliliter.

Problem Title - Radium Analysis Methods
 Report By - W. H. Power and W. C. McCluggage
 Work Done By - M. F. Hauenstein and W. C. McCluggage

INTRODUCTION

Since satisfactory methods of radium analysis will be required during both the research and pilot plant stages of the radium program, a review of the methods of radium analysis has been made. Different phases of the program will likely require different methods, since each has its own peculiar advantages and disadvantages. Factors which influence the choice of a method are the quantity of radium to be measured, the dilution of the radium, the accuracy and speed required, and the chemical and physical nature of the sample.

Radiometric analysis of radium is complicated by its many active daughters. These may either be allowed to come to equilibrium with the parent radium or separated to allow a count of radium alone. Also, the gaseous nature of radon makes a separation of this daughter a convenient method of evaluating radium.

Questionable geometry and self-absorption defeat attempts to calculate an accurate radium content from measured counting rates and known disintegration rates of radium and its descendants. All precision methods for radium analysis depend upon calibration against standard samples obtained from the National Bureau of Standards. These standards consist of sealed glass capsules containing several milliliters of aqueous

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solution of specified radium content, certified accurate to 0.1 per cent. The standardization of these solutions is based on gamma radiation comparisons with weighed radium.¹

Calorimetry

The calorimetric method has no immediate interest for radium evaluation since its application does not extend to the low level range. A 30-day stand period in a sealed container would be required for attainment of equilibrium before the method could be applied. Also, the incomplete absorption of gamma rays would make calculation of radium content from calorimetric data difficult.²

Electroscope

Davis (National Bureau of Standards) reports that the electroscope, either the gold leaf or the Wulf string type, still remains the best instrument for measurements of relatively large quantities of radium. The gold leaf electroscope is excellent for quantities over one milligram of radium, while the Wulf string type is very useful for quantities over 10^{-6} grams.⁴ Here again equilibrium conditions are necessary, and adsorption must be considered before measurement can be significant. The activity level required for these instruments is above that of immediate interest for the radium project.

Gamma Counting

Gamma counting for radium quantities in excess of 10^{-7} grams is a convenient method which also can be quite accurate if proper precautions are taken to account for absorption, to calibrate with a standard sample of the same order, and to await equilibrium conditions. Good checks of

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National Bureau of Standards values of radium contents in the range of one microgram have been reported by the Physics Section when using the gamma counting technique.⁵

The counting rate meter is also useful for rapid quantitative work with the Geiger tube.

Alpha Counting

Chloride Precipitation - Since most conventional methods of radium analysis require long time periods for attainment of equilibrium or for the growth of radon gas, these would be inconvenient for use as control methods for radium processing. The chloride precipitation method is designed to yield results within 30 to 60 minutes.⁶ Radium and barium chlorides are separated from other alpha active materials by precipitation in cold hydrochloric acid-ether solution. The washed precipitates are dissolved in nitric acid, transferred to a glass slide, and sulfuric acid is added to precipitate the radium and barium uniformly. The sample is dried under a heat lamp, ignited to volatilize polonium and counted in a parallel plate chamber. The range of application is limited by interfering activities to a minimum of 10^{-10} grams of radium per milliliter. This method may prove useful for the radium processing program and will be investigated.

Aeration - Another alpha counting method depends upon practical elimination of radon and its daughter products from radium samples by aerating for at least five hours during which time the radon is swept away and its short lived daughters decay.⁷ The authors state that because of the difficulty in concentrating radium without excessively increasing the

self-absorption of the preparation, the aeration method has been successfully applied only to pure solutions of radium and its decay products. Organic material may be burned off during the ignition step.

Beta Counting

A method which is applicable to biological materials is based on the coprecipitation of radium with barium sulfate after radon has been removed by heating the radium in solution.⁷ The radon and short-lived daughters reach equilibrium within the barium sulfate crystals. After a three-day growth period, beta particles from radium B and radium C are counted and compared with standard samples. The authors state that large errors may be encountered because of self-absorption unless one measures and corrects for the solid content of the capsules.

Radon Emanation Method

The most generally applicable method for radium analysis is the emanation technique in which the radon generated by radium is separated, collected, and measured. This method is especially useful for small quantities of radium because of its high sensitivity. Since a quantitative separation of gaseous radon is possible from any mass which can be dissolved, the final measurement is independent of the original bulk of material and is also independent of any radioactive materials other than radon and its daughters.

Techniques for evaluating the radon content include the following.

Ion Current Measurement - The ion current caused by all ionizing events between the center high potential electrode and the walls of the chamber containing radon is measured by an electroscope or an electrometer.⁴

The Wulf electroscope is capable of measuring as low as 5×10^{-11} grams of radium³ and a high sensitivity string electrometer can detect as little as 10^{-14} grams of radium. Obtaining such sensitivity by a direct ion current measurement is a difficult and exacting task.⁸ Since very high resistant circuits may be used, insulation problems are acute. The highest quality insulators must be used, humidity and temperature must be controlled, voltages must be stabilized and calibrated, a separate chamber must be provided to compensate for ionizing events from external causes, and elaborate photographic recording devices must be used for low-level determinations. Since all ionizing events contribute to the total current measured, calculation of the radon content from the ion current is more complex than calculation from a measurement involving only alpha particles from the decay of radon and its daughters. The change of capacity of the system with sensitivity also complicates calibration and computation. It is necessary to calibrate the instrument at all sensitivities.

Alpha Pulse Count Using the Ionization Chamber - This method is generally conceded to be the best radon measuring technique.^{1,8,9,10} The equipment is simpler, more rugged, and the conditions for low level radon measurement are much less critical than for the method utilizing ion current measurement. Instead of integrating current pulses caused by individual ionizing events, each event above a lower level of noise and gamma and beta pulses is amplified and individually recorded by a scaling circuit. For lowest level operation (less than 10^{-11} grams of radium) an automatic recorder can easily be arranged by coupling a commercial traffic recorder

to the scaling circuit output. All electrical parts for the system except the ionization chamber itself are commercially available. For samples above the lowest levels a reproducibility of the order of one per cent has been reported.^{1,8}

The Health Instrument Section at Mound Laboratory has installed an ionization chamber pulse counting apparatus for measuring the radon content of breath samples. Preliminary tests indicate satisfactory operation.¹¹

Alpha Pulse Count Using the Proportional Counter - This method utilized a counter operating in the proportional region to measure alpha pulses from radon disintegration.^{12,13} The high magnitude of electronic amplification required for the measurement of ionization chamber pulses is not necessary because of the gas amplification in the proportional chamber. Pulses caused by alpha particles can be differentiated from those caused by gamma rays and beta particles by selecting a suitable anode potential plateau which is below the required voltage for gamma or beta counting. Since the proportional counting technique is not established, the method is essentially in its development stage.

A proportional counter apparatus has been installed by the Chemistry Section.^{13,14} Although the instrument has been in operation for three months, conditions for consistent results have not yet been found.

Although the proportional counting method eventually may be as satisfactory as the ionization pulse counting method, more research work must be done to establish a satisfactory manifold system, counting gas, and operating technique. It is felt that traces of counting gas

impurities such as oxygen, water vapor, nitrogen, or carbon dioxide dampen proportional counting to a much greater extent than ionization pulse counting. Increased precautions must be taken to eliminate gas impurities when filling the proportional counter and to effect a complete transfer of radon.

DETAILED REPORT

Radon Counting by the Proportional Chamber

The proportional counter described in the previous report^{13,14} was tested with standard radium samples obtained from the Nation Bureau of Standards. Initial results were practically negative, since less than one per cent of the expected count was realized for samples of the order of 10^{-8} grams of radium. The counter operation was checked by placing solid alpha slides in the counting chamber and flushing with P10 gas (95 per cent argon and 5 per cent methane). Consistent alpha plateaus were obtained between 1,100 and 1,225 volts. The effectiveness of the dry ice traps for removing water vapor was then tested by making blank runs with water instead of radium solution, but keeping the solid alpha source in the counting chamber. The severely depressed plateau, illustrated by Figure 1, explained the poor results when counting radon gas. Traces of water vapor were apparently getting through the traps, into the counting chamber and damping the counting characteristics. Various water absorbants were tried including concentrated sulfuric acid, Drierite, anhydrous magnesium perchlorate, phosphorous pentoxide, tetraphosphoric acid, and different types of dry ice traps. The most effective improvement was obtained when a copper coil dry ice trap was substituted for a straight glass trap in

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order to provide more surface and better heat conductivity. When the new dry ice trap was used, good plateaus could be obtained when testing the apparatus with an inactive water sample and a solid alpha source.

Although more effective water vapor trapping improved the operation of the radon counter, results were still very low and inconsistent. Since mercury vapor would damp the count if any entered the counting chamber, the mercury manometer was replaced by a Bourdon gauge, and a Pirani gauge was installed to test the manifold for air leaks. Results with standard radium samples continued to be poor.

It was noticed that water samples, flushed with P10 and sealed overnight, gave poor results when the apparatus was being tested with dry alpha slides, but counts were satisfactory if a freshly flushed water sample was used. This observation suggested that traces of air leaking into the radon collection flask were shifting the counter plateau characteristics. Henceforth, radon collection flasks were kept under positive P10 pressure while cooling after refluxing to minimize leakage of air into the flask. Although sealing radon collecting flasks under positive P10 pressure improved the count with known radium samples considerably, results continued to be inconsistent. The recommendation of Curtiss⁸ of employing a hot copper trap for removing traces of oxygen was followed. A Pyrex tube containing copper turnings heated to 435° was placed between the first and second dry ice traps. Suitable stopcocks were provided to regenerate the copper with hydrogen after every run in order to assure maximum capacity and to recognize the presence of oxygen in a sample by the degree of tarnishing of the copper. After the installation of the copper trap

additional improvements in results were noticed, but consistent checks were still not obtained. From 22 to 80 per cent of the expected radon count was obtained when testing the apparatus with standard radium samples containing 10^{-9} grams of radium. Since low counts were usually associated with severe tarnishing of the copper, nitrogen was intentionally introduced into the system to determine if that gas would dampen the counting characteristics of the proportional counter. The behavior of the counter when $3\frac{1}{2}$ and 7 per cent of nitrogen were added to the counting gas is illustrated by Figure 2. Decided plateau shifts were caused by nitrogen, so removing only oxygen from air contaminating the counting gas was not sufficient.

It is hoped that nitrogen gas may be used as a counting gas instead of P10. If so, a combination of the copper trap and dry ice traps should remove all materials causing damping of the proportional counter.

If a counting medium can be found which is not critically affected by traces of air or moisture, the problem of obtaining consistent results will be that of effecting a quantitative transfer of radon to the chamber. The possibility of making a quantitative transfer of radon will be greater if the volume ratio of the counting chamber to the manifold and emanation flask is large. For the latest design the counting chamber has a volume of 1,960 cubic centimeters and the manifold plus emanation flask 1,223 cubic centimeters. Any change in design which will reduce the latter volume will improve the possibilities of obtaining a consistent complete transfer of radon.

Alpha Counting - Aeration Method

The method of Tompkins⁷ for radium analysis by alpha counting has been investigated. The method consists of removing radon and its short-lived daughters from a radium solution by aeration for more than five hours, preparing an alpha counting slide on platinum, igniting to volatilize polonium, and counting immediately. This method has been tested and found to give good results if the radium sample does not contain excessive solid material which causes absorption loss. Results of counting a sample of radium chloride solution by the aeration method are given in Table II.

Attempts were made to find a less expensive mounting material than platinum and to obtain good counts from solutions with high organic content. From the standpoint of preparation and ignition, platinum is a very satisfactory slide material. A 100-lambda sample can be easily placed on a 7.8-inch disc. It dries evenly under the heat lamp and adheres well upon final ignition over a microburner.

When using ordinary glass alpha slides, the sample tends to flow toward the edges. This difficulty may be overcome by coating the edge of the slide with a narrow band of "Strip-Film" which may be removed by mild ignition.

A mixture of radium and polonium was counted by the Tompkins method in order to check on the removal of polonium by ignition. That glass is a more satisfactory material for polonium removal than platinum is indicated by the results mentioned by Table III. It is known that polonium may not be completely removed from platinum by ignition, probably because of diffusion of the metals and compound formation.

When analyzing radium solutions passed through an ion exchange column, the problem arose of removing organic materials from the slide in order to prevent excessive absorption. The residue from evaporation of a citrate solution is a syrupy layer which must be ignited before the slide can be counted. After ignition inorganic residues which are not very adherent on glass may be fixed in place by applying a drop of collodion.

Nickel discs were tried for nitrate solutions without success. There was some evidence that nickel is useful for chloride solutions.

REFERENCES

1. Fineman, P., et al., National Nuclear Energy Series IV-14B, p. 1206 (1949).
2. Eichelberger, J. F., Personal Communication.
3. Davis, F. J., J. Assoc. Offic. Agr. Chemists, 28, 682-684 (1945).
4. "Methods of Analysis" A.O.A.C., 552 (1940).
5. Eyles, T. E., Personal Communication.
6. Ames, D. P., et al., National Nuclear Energy Series IV-14B, p. 1700 (1949).
7. Tompkins, P. C., et al., MDDC-699 (1946).
8. Curtiss, L. F. and Davis, F. J., RP 1557, J. Research of Nat. Bur. Standards 31, 181-95 (1943).
9. Jacobi, R. B., Chem. Soc. Supp. Issue No. 2, S 314 (1949).
10. Thomas, H. C. and Tomcufcik, A. S., Off-Project Classified Document M-2762.
11. Miller, R. A., Personal Communication.

12. Brown, S. C., Elliott, L. G., and Evans, R. D., Rev. Sci. Inst.
13, 147-51 (1942).
13. Ohmart, P. E., Quarterly Report for General Research, MLM-443-1.
14. Power, W. H., Quarterly Report for General Research, MLM-443-1.

Table I
RADIUM ANALYSIS METHODS

	<u>Lower Limit Grams of Radium</u>	<u>Time Required for Analysis</u>	<u>Estimated Reproducibility Per Cent</u>
1. Calorimetry	10^{-2}	*	1
2. Electroscope			
Gold Leaf	10^{-3}	*	
Wulf String	10^{-6}	*	
3. Gamma Counting	10^{-7}	*	1
4. Alpha Counting			
Chloride Precipitation	10^{-10}	1 Hour	3-10
Aeration Method	10^{-11}	6 Hours	
5. Beta Counting	5×10^{-9}	3 Days	
6. Radon Emanation Method			
Ion Current Measurement	10^{-13}	18 Hours	
Ion Pulse Counting	10^{-13}	18 Hours	2
Proportional Counting	10^{-13}	18 Hours	

* Method requires that radium sample be sealed for 30 days to attain equilibrium.

Table IIRADIUM ALPHA COUNTING BY AERATION METHOD

<u>Slide Material</u>	<u>c./min./slide</u>	<u>Ignition</u>	<u>Remarks</u>
Platinum	244	Heat lamp and microburner	The average count of 249 taken as reference.
Platinum	249		
Platinum,	254		
Glass	170	Heat lamp only	
Glass	152		Low count due to self-absorp- tion. The average count of 242 compares well with Pt Simpson slides used.
Glass	245	Heat lamp and slow ignition	
Glass	241	on asbestos	
Glass	239		
Glass	240	Heat lamp and slow ignition	
Glass	242	on asbestos	
Nickel	90	Heat lamp and microburner	The residue ignited so rapidly part of it was lost. This residue was a nitrate.
Nickel	95		
Nickel	82		

Table IIIREMOVAL OF POLONIUM BY IGNITION OF SAMPLE ON PLATINUM AND GLASS SLIDES

<u>Slide Material</u>	<u>c./min./slide</u> <u>Ra + Po</u>	<u>Remarks</u>
Platinum	246	These slides were ignited for one minute at red heat. The average count is 266 as compared to an average of 249 for Ra only
Platinum	268	
Platinum	286	
Glass	237	These slides were dried then heated on an asbestos gauge over a Fisher burner. The average count is the same as that for Ra only.
Glass	243	
Glass	246

EFFECT OF NITROGEN ON PROPORTIONAL
COUNTER PLATEAU

Problem Title - Chemical Engineering Development of the Radium Process
(Area 1-C, Semiworks Building)

Report By - T. H. Coffing, J. A. Rauscher, and H. L. Rawlings

Work Done By - T. H. Coffing, J. A. Rauscher, and H. L. Rawlings

INTRODUCTION

The design of the Semiworks Building shell has been completed. It is felt that the area assigned to radium separation is sufficient and of usable dimensions.

A temporary organization was set up to design the Pilot Plant equipment with the Research Division furnishing chemical engineers, the Engineering Division the draftsmen and other engineers. The time schedules and cost estimates were brought up to date; two more chemical engineers have been assigned to the problem.

The chemical engineering is proceeding satisfactorily on the K-65 residue treatment process. Only limited information is, as yet, available on the radium-barium separation process.

DETAILED REPORT

Standard data and instruction sheets have been prepared to collect engineering data for the selection of suitable filters, centrifuges, reactors, tanks, pumps, valves, piping, etc. The purpose of these data sheets is to form a basis for engineering design, and a record of the information available for the design, of pilot plant equipment.

The proposed Semiworks Building is to house pilot plants for radium, actinium, and waste disposal processes. The drawings prepared by the Engineering Division were checked to make sure that the present needs were met and also that the building would be suitable for a future pilot plant.

The proposed radium area will comprise a space 30 by 140 feet with 24 feet of clear head room which is one-half of the Semiworks Building. The area will be provided with 10 changes of unfiltered air per hour with down-draft ventilation to prevent active dust from being carried off the floor. The entering air will be tempered by steam coils and localized heating provided with space heaters.

The concrete floors will be pitched toward drainage trenches running along the walls which conduct the water to three sumps. The waste water will be pumped to processing tanks before being discharged to the sewer.

A balcony 17 feet wide and 16 feet above the operating floor will run along the outside wall to provide gravity feed for solids between filters or centrifuges and the reactors.

The entire area will be served by a two-ton, overhead crane. Steam, water, electrical power, and compressed air will be supplied by the plant system; vacuum will be supplied locally.

Objectives were set for the chemical engineers working on the radium process. In general, data gathered from the research chemists is to be expressed in complete equipment flow sheets. This will involve also the choice of the best equipment for the various duties, plus complete specifications and purchase requisitions for all equipment.

Organization of the Problem

Two time estimates for the radium project are being issued twice monthly by this group. The first estimate shows completion times and manpower needed, both engineering and drafting, to accomplish the necessary work at given times. The second estimate is somewhat simpler, showing only completion times. This second estimate will be attained only if the necessary quality and quantity of personnel are available as needed.

A new cost estimate was made to cover items which were not estimated in either the building shell or the equipment proposals. Another estimate, corrected to June 21, was made of the process equipment cost.

A trip to Mallinckrodt Chemical Company provided information on the K-65 residue and methods of handling by Mallinckrodt.¹ Of note is the fact that the K-65 residue is packaged in 55-gallon drums containing 500 pounds of wet residue with 50 to 65 milligrams of radium and a moisture content of about 30 per cent. We propose to process a maximum of one drum of residue per eight-hour day in the pilot plant.

The radium program has been divided into three parts of approximately equal magnitude.

1. K-65 residue treatment (to obtain a pure mixture of radium and barium). The chemical engineering is approximately 50 per cent complete on this part; no drafting has been done as yet.

2. Separation of radium from barium. Very little chemical engineering and no drafting has been done.

3. By-product handling and waste disposal. Very little chemical engineering and no drafting has been done.

A successful K-65 residue treatment process has been developed by the research chemists, and data sheets for most of the steps are available for engineering of the process.

1. Heat transfer, material balances, and equipment sizes have been calculated and checked.
2. Evaluation of alternate process equipment is being conducted.
3. A preliminary flow sheet is about 70 per cent complete.

REFERENCE

1. Rauscher, J. A., Notes on the Trip to Mallinckrodt Chemical Co. on June 2, 1950.