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AND RADIOCHEMISTRY

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REPORT

FOR

GENERAL RESEARCH

JUNE 26 TO SEPTEMBER 18, 1950

(Radium Volume)

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(Radium Volume)

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SUMMARY

The purpose of the research work reported in this volume is the development of a process for the separation and subsequent purification of radium from the K-65 (pitchblende) residue. The results reported have made it possible to define the operations to be employed. It is expected that the next quarterly report will conclude the laboratory research work and make available details necessary to carry out pilot plant studies with engineering equipment.

The first step in the process is the extraction of about 85 per cent of the lead and about 40 per cent of the silica content with a 15 per cent sodium hydroxide solution (14). The use of Versene solutions (9) and sodium chloride solution (11) for the preliminary extraction step were found to be less desirable than the sodium hydroxide procedure.

After the sodium hydroxide extraction, the residue is treated with a solution containing both sodium hydroxide and sodium carbonate. This procedure combines into one operation a second sodium hydroxide extraction and conversion of the barium-radium sulfate to carbonate. In addition to eliminating the number of operations, the combined reaction provides better lead removal and more complete conversion to the carbonate. After the first extraction of the radium and barium with nitric acid, a second carbonation and extraction is made. Based on the recovery of barium, the extraction appears to be complete. About two per cent of the lead follows the radium-barium extract. Preliminary experiments have shown that higher carbonate conversions can be achieved at increased temperature and pressure, but the work has not been extended to the K-65 residue (14).

[REDACTED]

After the removal of the lead by sulfate precipitation and further purification by precipitation of the barium-radium carbonates, the radium is concentrated by fractional chromate precipitation. Experiments have shown that the rate of concentration can be predicted on the basis of the theoretical separation factors (35). Although the final fractionation scheme has not been established, it appears much superior to the fractional crystallization method (27).

The radium-rich barium chromate can be dissolved in nitric acid and absorbed on the top of an ion exchange column (51) and the radium is then separated by elution of the column with ammonium citrate solutions (59).

A two-step process for the decontamination of waste solutions has been worked out. The major portion of the activity is carried down by lead sulfate which precipitates when the sodium hydroxide leach is mixed with other waste solutions and neutralized. The filtrate is further decontaminated by precipitation of ferrous ferrocyanide (73).

The chemical engineering of the Radium Process has been shifted from the design of a producing pilot plant to bench-scale development. How far this work will continue has not been determined (100).

Problem Title - The Solubility of K-65 Residues in Versene
Report By - J. G. Stites
Work Done By - J. G. Stites

INTRODUCTION

The radium recovery process for the most part involves the removal of certain divalent metallic ions from K-65 residues. A complexing agent specific for divalent ions would be an ideal substance for use in this case. Versene, the sodium salt of ethylenediaminetetracetic acid, closely approaches the prerequisites for the removal of lead, barium, and radium ions, consequently, several experiments have been run to test this compound.

DETAILED REPORT

Lead sulfate is soluble in Versene to the extent that one gram of the sulfate requires seven milliliters of liquid Versene for complete solution. This observation is of no particular significance since the lead sulfate would also be soluble in the amount of sodium hydroxide which is present in the Versene. Barium sulfate is not soluble in Versene unless there is a large excess of carbonate present.

In K-65 residues there is approximately twice as much lead as there is barium. To a mixture of two grams of lead sulfate and one gram of barium sulfate was added 50 milliliters of Versene and 12 grams of potassium carbonate. The mixture was boiled for 15 minutes and then filtered. There was 0.3 grams of residue which was analyzed and found to be barium sulfate.

These data indicated complete solution of the lead sulfate and 70 per cent solution of the barium sulfate.

A series of experiments similar to the one run on the barium sulfate: lead sulfate mixture was performed using K-65 residues. The results of these experiments are tabulated below:

Exp.	K-65 (grams)	K ₂ CO ₃ (grams)	Versene (ml.)	H ₂ O (ml.)	Time Boiled (min.)	Insol. Residue (grams)	SiO ₂ (grams)	Filtrate	BaSO ₄ (grams)
								PbSO ₄ (grams)	
I	5	5	10	10	15	2.36	0.814	1.15	0.034
II	5	2.63	10	10	30	2.53	0.73	1.0	0.075
III	5	0	10	10	30	2.54	0.70	0.77	0.013

The amount of radium found in the Versene extracts was very small. The aeration method of analysis did not allow an accurate determination of the amount present, however, from rough calculations it can be shown that the barium:radium ratio was probably the same in both filtrate and residue.

From the results of the experiments it can be concluded that the use of Versene would not be of any particular benefit. The lead can be extracted with sodium hydroxide. The barium was extracted to such a small extent that the use of Versene would be impractical.

Problem Title - The Extraction of Lead from K-65 Residues by Sodium Chloride
Report By - J. G. Stites
Work Done By - J. G. Stites and M. Economides

INTRODUCTION

The extraction of lead from K-65 residues using saturated sodium chloride solution has been studied. The preliminary work on this study was reported in the last Quarterly Report.¹

DETAILED REPORT

No lead was extracted from K-65 residues by saturated sodium chloride solution unless the mixture was made slightly acid. A water suspension of K-65 residues is slightly alkaline (pH 9).

In general, the procedure for the extraction of lead entailed adding K-65 residues to a known concentration of sodium chloride, adjusting the mixture to pH 4 by the addition of dilute hydrochloric acid, boiling for one hour, and then filtering. The lead was recovered from the filtrate by diluting and adding an excess of sulfuric acid. The resulting precipitate of lead sulfate was dried and weighed.

The residue from the sodium chloride extraction was washed thoroughly and dried before weighing.

The data obtained from some of the experiments are tabulated in Table I. From examination of these data it can be concluded that for maximum efficiency of extraction solid sodium chloride must be present during

the digestion. The best conditions obtained still yielded only an 80 per cent extraction of the lead sulfate. This is not an improvement over the sodium hydroxide extraction.

A study was made on the carbonation of the sodium chloride residues. The best results indicated only a 63 per cent removal of barium on the first carbonation. A minimum of approximately 80 per cent of the barium is removed by the carbonate treatment of K-65 residues which have been extracted with sodium hydroxide.

Sodium chloride does not remove any of the silica present in the K-65 residues. The silica caused some interference during the carbonation since it reacted with some of the sodium carbonate and, also, since it interfered to some extent with the subsequent filtration.

Sodium hydroxide seems to be the better reagent to use for the removal of lead from K-65 residues.

REFERENCE

1. Report for General Research, MLM-475, 70A-D, April 1 to June 26, 1950.

Table I

DATA FROM SODIUM CHLORIDE EXTRACTION OF LEAD FROM K-65 RESIDUE

<u>Exp.</u>	<u>K-65</u> <u>(grams)</u>	<u>NaCl</u> <u>(grams)</u>	<u>H₂O</u> <u>(ml.)</u>	<u>Wt. of</u> <u>Residue</u> <u>(grams)</u>	<u>Total</u> <u>Extract</u> <u>(grams)</u>	<u>PbSO₄</u> <u>(grams)</u>	<u>Extracted</u> <u>Per Cent</u>
I	100	414*	1200	80.8	19.2	11.06	46.3
II	100	487**	1200	77.5	32.5	13.51	58.2
III	101.5	487***	1000	72.9	27.1	19.3	80.7

* Saturated with NaCl at 25°.

** Saturated with NaCl at 100°.

*** Excess NaCl present.

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

Report By - E. F. Joy

Work Done By - E. F. Joy

INTRODUCTION

One of the principal problems met with in the recovery of a barium-radium concentrate from K-65 residue has been the preliminary separation of lead. The carbonation of the residue to convert the barium and radium to carbonates is relatively straightforward providing the lead content has been reduced to a sufficiently low value. The conversions obtained improve as the lead content decreases, and the purity of the barium-radium sulfate recovered is, of course, higher. The removal of at least 95 per cent and preferably 98 per cent of the lead is desirable at this point to avoid throwing too heavy a burden on the final purification of the barium-radium concentrate by precipitation of sulfides.

The results previously reported¹ on the extraction of lead from K-65 residue show that about 85 per cent of the lead can be extracted in a single treatment with 15 per cent sodium hydroxide in a ratio of 2 grams of sodium hydroxide per gram of lead sulfate. About 40 per cent of the initial silica is also dissolved. Increasing the excess of sodium hydroxide used in a single treatment does not appreciably increase the amount of lead extracted. A small increase is obtained by carrying out the extraction in two steps. It seems likely that the remaining lead is held more tightly in the residue perhaps as a basic lead silicate rather

[REDACTED] [REDACTED]

than lead sulfate. On carbonation of this residue followed by solution in dilute nitric acid, essentially all of the lead is dissolved but is recovered as a contaminant in the barium-radium sulfate precipitated from this solution.

Consideration was given to the possibility that the carbonation step followed by a second treatment with sodium hydroxide would convert the residual lead first to carbonate then to soluble plumbite which could be separated from the barium. Extraction of the carbonated residue with nitric acid would then give a barium-radium solution reasonably free from lead. This possibility has been investigated along with the alternative of combining the sodium carbonate and sodium hydroxide treatments in a single step for the same purpose. The results of these experiments and of preliminary study of the carbonation reaction under pressure are given in the detailed report.

DETAILED REPORT

An initial treatment of the K-65 residue with sodium hydroxide solution was selected as the first step in each of the experiments planned. By treating a large sample of K-65 (1,000 grams in two 500-gram batches) a uniform sample of residue was obtained from which the bulk of the lead had been extracted. Comparison of alternative methods of combining the subsequent carbonation and sodium hydroxide leaches could then be made by treating equal portions of this residue. In Table IA the reagents used and the order of treatment is summarized. The initial sodium hydroxide treatment is numbered 8-1 and 8-2. The washed and dried residues from

[REDACTED]

[REDACTED] [REDACTED]

these two leaches were combined to give a uniform sample of 528.5 grams. This sample was divided into five equal portions, each equivalent to 200 grams of original K-65. The treatment of three of these portions was carried to completion as Experiments 8A, 8B, and 8C as outlined in the remainder of the table.

The normal order of treatment was followed in 8A. In 8B the first treatment with sodium carbonate preceded the second sodium hydroxide treatment. In 8C the sodium carbonate for the first treatment and the sodium hydroxide for the second treatment were combined in a single solution, giving one less step in the overall sequence. It should be noted that the same total amount of reagents was used in each of the alternative procedures. The total sodium hydroxide used was based on the minimum requirements for dissolving lead sulfate (2.1 grams of sodium hydroxide per gram of lead sulfate) plus the stoichiometric amount for dissolving 40 per cent of the silica originally present. The sodium hydroxide was taken as a 15 per cent solution and leaching was carried out at 95 to 100° for 1 1/2 hours. Sodium carbonate was taken on the basis of 5 moles of sodium carbonate per mole of barium sulfate and made up as a 20 per cent solution. Leaching time was 2 hours at 95° to 100°. Experiment 9 is a duplicate of 8C on a larger scale. In this experiment 500 grams of K-65 was carried through the whole procedure with the same ratio of reagents.

The results obtained are summarized in Tables IB, IC, and ID. The distribution of lead in the various filtrates is given in Table IB. The bulk of the lead, of course, was found in the first sodium hydroxide leach.

[REDACTED]

The combined sodium hydroxide-sodium carbonate treatment, Experiments 8C and 9, was found to remove more of the lead than either of the separate treatments. Sodium carbonate treatment before the second sodium hydroxide, Experiment 8B, is somewhat better than the reverse order, Experiment 8A. The total lead recovered shows some variation which is attributed in part to difficulties experienced in the analysis of lead in these samples. The summary indicates that 97 to 98 per cent of the lead can be removed by the combined treatment leaving less than three per cent of the lead in the barium sulfate which is recovered.

The recovery of barium sulfate is summarized in Table IC based on the analysis of the nitric acid solutions from which barium sulfate was precipitated. The best recoveries were obtained in Experiments 8C and 9 using the combined sodium hydroxide-sodium carbonate treatment. The figures exceeding 100 per cent are not out of line with more recent analyses for barium sulfate in K-65 which indicate a higher content than the 9.67 per cent on which these per cent recoveries are based.

The distribution of silica in the sodium hydroxide and sodium carbonate solutions is given in Table ID. No significant difference in the per cent silica extracted was noted among the various procedures.

Summarizing the results of these experiments, it seems clear that combining the sodium carbonate and sodium hydroxide leaches as indicated has certain advantages. Better extraction of lead and higher yields of barium sulfate were obtained with one less step in the procedure. The effect may be due in part to the higher effective salt concentrations.

This phase will be clarified when concentration studies are made on the carbonation of K-65 with the Pfaudler autoclave.

Carbonation of Cold Barium Sulfate under Pressure

The study of the carbonation reaction was extended to temperatures above 100° in the 1-gallon experimental Pfaudler autoclave. The autoclave is equipped with a stainless steel removable liner and an anchor type motor-driven agitator. The effect of temperature on the per cent conversion of barium sulfate to barium carbonate was studied in the range of 110° to 170°. Other conditions were kept the same as in the previous studies at 100°, i.e., concentration of sodium carbonate, molar excess, and time at reaction temperature.

The procedure followed in each experiment was to transfer the barium sulfate to the liner as a slurry and add the remaining water and the sodium carbonate to give the proportions of reactants indicated in the first part of Table II. The cover of the autoclave was then lowered into place with a small hand hoist and bolted down. The autoclave was heated externally with a gas burner leaving the vent valve open until the temperature reached 100° and the air had been swept out of the autoclave by steam. The valve was closed, and the autoclave was brought to the reaction temperature. After two hours at this temperature the heat and agitation were cut off, and the autoclave was allowed to cool to 100°. The autoclave was then opened, and the liner with contents were removed. The settled reaction mixture was filtered and the residue washed by decantation and on the filter. The carbonated cake was dissolved in dilute hydrochloric

acid, and the unconverted barium sulfate remaining was filtered out, washed, ignited, and weighed. The results are given in Table II and Figure 1.

The conversion of barium sulfate to carbonate was increased from 89 per cent at 100° to better than 99 per cent at 170°. A further slight increase in conversion could be obtained by increasing the temperature above 170° although the gain hardly appears worthwhile. The equilibrium constant for the carbonation reaction:

can be expressed in terms of molal concentrations of the ions involved as

$$K = \frac{[\text{SO}_4^{=}]}{[\text{CO}_3^{=}]}$$

K was calculated for each of the temperatures and gave values from 0.217 to 0.248 increasing with temperature as would be expected.

Data in the literature on the equilibrium constant for the carbonation reaction are contradictory. Guldeberg and Waage² are reported to have obtained values for K of about 4.0 under unspecified conditions. Meyerhoffer³ found that the value of K varied not only with temperature but also with the concentration. Latimer and Hildebrand⁴ report a value of about 0.01 for K in 1 molar sodium carbonate solution.

Further study of the carbonation of cold barium sulfate with sodium carbonate solutions of higher concentration up to about 30 per cent are planned after which the carbonation of K-65 residue under pressure will be attempted.

REFERENCES

1. Joy, E. F., Quarterly Report for General Research, MLM-475, p. 36.
2. Glasstone, "Textbook of Physical Chemistry," 2nd Edition, p. 852.
3. Meyerhoffer, W., Zeit. phys. Chemie., 53, 603 (1905).
4. Latimer, W. and Hildebrand, J. H., "Reference Book of Inorganic Chemistry," Revised Edition, p. 73.

REAGENTS USED AND ORDER OF TREATMENT

<u>First Sodium Hydroxide Treatment</u>						<u>Subsequent Treatment of the Residue</u>						
<u>Experi-</u> <u>ment</u>	<u>K-65</u> <u>Sample</u> <u>grams</u>	<u>NaOH</u> <u>grams</u>	<u>H₂O</u> <u>grams</u>	<u>Residue</u> <u>grams</u>	<u>Total</u> <u>8-1 &</u> <u>8-2</u> <u>grams</u>	<u>Residue</u> <u>Sample</u> <u>grams</u>	<u>Equi-</u> <u>valent</u> <u>K-65</u> <u>grams</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
8-1	500	250	1417	264.0	528.5							
8-2	500	250	1417	264.5								
8A						105.7	200	50 g. NaOH(2) 284 g. H ₂ O	45.4 g. Na ₂ CO ₃ (1) 182 g. H ₂ O	HNO ₃ (1)	45.4 g. Na ₂ CO ₃ (2)	HNO ₃ (2)
8B						105.7	200	45.4 g. Na ₂ CO ₃ (1) 182 g. H ₂ O	50 g. NaOH(2) 284 g. H ₂ O	HNO ₃ (1)	45.4 g. Na ₂ CO ₃ (2)	HNO ₃ (2)
8C						105.7	200	45.4 g. Na ₂ CO ₃ (1) 50 g. NaOH(2) 257 g. H ₂ O	HNO ₃ (1)	45.4 g. Na ₂ CO ₃ (2) 182 g. H ₂ O	HNO ₃ (2)	
9	500	250	1417	n.d.		All	500	110 g. Na ₂ CO ₃ (1) 125 g. NaOH(2) 640 g. H ₂ O	HNO ₃ (1)	110 g. Na ₂ CO ₃ (2) 440 g. H ₂ O	HNO ₃ (2)	
n.d. = not determined.												
(1) and (2) indicate the first or second treatment												

n.d. = not determined.

(1) and (2) indicate the first or second treatment of the residue with the reagent in question.

20

Table IB

DISTRIBUTION OF LEAD

<u>Experiment</u>	<u>Grams of Lead</u>							<u>Pb % Recovery**</u>	<u>Summary</u>	
	<u>1st NaOH</u>	<u>2nd NaOH</u>	<u>1 Na₂CO₃</u>	<u>1st HNO₃ (BaSO₄)</u>	<u>2nd Na₂CO₃</u>	<u>2nd HNO₃ (BaSO₄)</u>	<u>Total</u>		<u>Lead Extracted*** in NaOH and Na₂CO₃ Solutions</u>	<u>Lead Left*** in BaSO₄</u>
8-A	28.36	2.87	0.32	1.43	nil	0.10	33.08	101.5	95.4	4.6
8-B	28.36	3.67	0.46	1.15	nil	0.15	33.79	103.7	96.2	3.8
8-C	28.36		5.06*	0.86	nil	0.05	34.33	105.2	97.4	2.6
9	68.4		7.58*	1.46	nil	0.19	77.65	95.25	97.8	2.2

* Combined NaOH-Na₂CO₃ solution.

** Based on lead analysis of K-65 - 16.3 per cent lead.

*** Expressed as per cent of total lead found.

Table ICBARIUM SULFATE RECOVERED - BASED ON ANALYSIS OF THE HNO₃ SOLUTIONS

<u>Experiment</u>	<u>1st HNO₃ BaSO₄ (grams)</u>	<u>2nd HNO₃ BaSO₄ (grams)</u>	<u>BaSO₄ Total (grams)</u>	<u>% Recovery</u>
8-A	12.90	5.62	18.52	95.8
8-B	13.40	5.05	18.45	95.4
8-C	18.94	1.05	19.99	103
9	45.2	11.2	56.4	110

Table IDDISTRIBUTION OF SILICA IN SODIUM HYDROXIDE AND SODIUM CARBONATE SOLUTIONS

(Data Expressed as % of the Total Silica Taken in the K-65)

<u>Experiment</u>	<u>1st NaOH</u>	<u>2nd NaOH</u>	<u>1st Na₂CO₃</u>	<u>2nd Na₂CO₃</u>	<u>Total</u>
8-A	41.1	2.89	0.60	0.99	45.58
8-B	41.1	2.94	1.37	0.43	45.84
8-C	41.1	3.92*		1.18	46.20
9	38.2	3.12*		0.59	41.91

* Combined NaOH - Na₂CO₃ solution.

Table II

PRESSURE CARBONATION OF BARIUM SULFATEEffect of Temperature on the Conversion

BaSO ₄ in Sample (grams)	200
Na ₂ CO ₃ in Sample (grams)	454
Molar Ratio Na ₂ CO ₃ /BaSO ₄	5
H ₂ O in Sample (grams)	1816
Na ₂ CO ₃ Concentration (%)	20

Experiment	Temperature of Carbonation (°C.)	Time to Reach Temperature (Hours)	Time at Temperature (Hours)	Pressure (p.s.i.g.)	Unconverted BaSO ₄ (grams)	Conversion (%)	K = $\frac{[SO_4]}{[CO_3]}$
10	170	1.45	2.0	93	1.65	99.2	0.248
11	150	1.33	2.0	49	2.26	98.9	0.246
12	130	0.70	2.0	20	4.70	97.6	0.243
13	110	0.53	2.0	<5	n.d.	95*	0.235
3	100	--	2.0	--		89	0.217

* Based on analysis for sulfate ion in the carbonate solution.

CONVERSION OF BARIUM SULFATE
TO BARIUM CARBONATE
EFFECT OF TEMPERATURE

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

INTRODUCTION

There are numerous reports in the literature^{1,2} on the separation of radium from barium. The method of separation in each account is essentially the same; namely, the fractional crystallization of the bromides from water or hydrobromic acid solutions. The degree of separation for the different methods varies somewhat, depending upon the solvent used. For maximum separation the optimum solvent has been found to be 0.33 normal hydrobromic acid.¹

DETAILED REPORT

A continuation of the work originally reported³ indicates that the partition factor, D, has a value of 15 when 0.33 normal hydrobromic acid is used. In Table I are listed the partition factors, D, which were obtained for four series of crystallizations. Each value was obtained in the same manner as outlined in the last Quarterly Report.³ This value of D drops to 10 when water is used as a solvent.

In spite of the added advantage of separation obtained by the use of hydrobromic acid as a solvent, the process lends itself better to continuous production when water is used as the solvent. This advantage is exemplified in Figures 1 and 2. (When water is used as the solvent, 33 1/3 per cent of the barium and 83 1/3 per cent of the radium crystallized

in each step.³⁾ Identical concentrations (barium to radium ratios) are made periodically. Such a phenomenon can be used to an advantage, since when the original concentration is obtained, more starting material can be added at that point. A scheme utilizing a partition factor of 10 and one in which the concentrations are repeated periodically is shown in Figure 1.⁴ This scheme does not entail a transfer of crystals but rather a transfer of mother liquor only. Starting material could be added every fifth crystallization.

Figure 2 exemplifies a scheme which requires two series of containers, each container of which will be designated to hold a definite radium to barium ratio. With this scheme it would be necessary to fractionate from one series of dishes to the other. This method of fractionation gives a maximum of separation in a minimum time since each fraction is crystallized every day.

When 0.33 normal hydrobromic acid is used as a solvent for the barium-radium bromides, the fractional crystallization becomes a batch process since there is no repetition of concentrations; i.e., once a fractionation is started there is no suitable place for the addition of more original material.

CONCLUSION

In spite of the fact that the use of 0.33 normal hydrobromic acid as a solvent for the fractional crystallization of barium-radium bromide mixtures affords a better separation, the use of water as a solvent gives a process which is more easily adaptable to continuous production.

A final report is in preparation in which sizes of vessels, amounts of materials, etc., are reported.

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p. 45.
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Table IPARTITION FACTORS FROM FRACTIONAL CRYSTALLIZATION OF RADIUM-BARIUM BROMIDE MIXTURES IN 0.33 NORMAL HYDROBROMIC ACID SOLUTION

<u>Series</u>	<u>I & II</u>	<u>II & III</u>	<u>III & IV</u>	<u>IV & V</u>	<u>V & VI</u>
1	14.0				
	14.3	5.6			
2	16.4				
	12.5	14.4			
3	10.7				
	35.4	10.4			
4	12.9				
	9.2	10.0			
	38.5	10.7	15.1		
	24.3	18.5	16.6	4.5	
	26.6	10.4	16.1	9.0	3.3

Av. D = 14.98

FIGURE 1

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FOR EXAMPLE: FOR ONE FRACTIONATION THE CRYSTALS FROM 1.0 GO TO 2.5
WHILE THE MOTHER LIQUOR WOULD BE POURED INTO 0.24

FRACTIONAL CRYSTALLIZATION SCHEME-SCHOLL.

FIGURE 2

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

INTRODUCTION

Many fractional methods have been reported for the concentration of radium from barium-rich mixtures, of which, the fractional precipitation of chromates has yielded the highest partition factors.¹ However, the fractional precipitation of chromates is difficult to control. Henderson and Krecek² dissolved barium-radium chromates in nitric and hydrochloric acids and precipitated a fraction of the chromates by neutralizing a portion of the acid with sodium hydroxide. Although individual experiments yielded chromates enriched in radium, they were unable to devise a fractionation scheme to compete with fractional crystallization. Murkulova³ made extensive studies of the distribution of radium between solid barium chromate and barium dichromate solutions. One of his many studies involved the saturation of nitric acid solutions with barium chromate, followed by the precipitation of a portion of the barium chromate with sodium hydroxide. Murkulova observed that even though the same amount of sodium hydroxide was added to each solution, the fraction of the barium chromate precipitated often varied tremendously. For example, in two experiments carried out in the same manner, he precipitated 6 per cent and 22 per cent of the dissolved barium chromates, respectively. In addition he found that the kind and time of stirring also affected the per cent of barium precipitated. It is obvious that no

systematic fractionation scheme could be developed with such erratic precipitation control. Regardless of this problem the high partition factors obtained by fractional chromate precipitations and the rapidity with which samples may be reworked cannot be disregarded. The following report deals with the development of a fractional chromate procedure for the concentration of radium from barium-rich mixtures.

DETAILED REPORT

Chromate-Urea Method

Barium chromate is an excellent carrier of radium chromate, hence, fractional precipitations of barium-radium chromates yield precipitates enriched in radium. In the previous Quarterly Report¹ a new method for the fractional precipitation of barium-radium chromates was suggested. It was observed that 95 per cent of the radium chromate will be carried from a nitric acid solution of barium-radium chromates if 50 per cent of the barium chromate is precipitated. This enrichment appeared to be a good working factor for a batch-wise procedure for the enrichment of radium.

The chromate-urea method differs from the older method² of fractional chromate precipitation in that the acidity of the solution is reduced by the hydrolysis of urea in boiling solutions instead of by the addition of sodium hydroxide. As is true for precipitations from homogeneous phase, the solid phase is very granular, making filtrations rapid and reducing the time of each fractionation step.

Henderson and Kracek² found that the enrichment of radium was improved if the fractional chromate-precipitations were carried out in

weakly acid solutions, but were hindered if the acidity was too high (more than 0.3 molar nitric acid). The optimum solvent appears to be a 0.25 molar nitric acid solution.

The principle problem in development of the chromate-urea procedure was the determination of a rapid and moderately accurate method for controlling the amount of barium chromate precipitated. Four proposed methods, color, reduction of half the chromate to a lower oxidation state, removal of half the chromate with lead, and a timed reaction, were investigated. Of these, only the last is practical. The color change of the solution produced by precipitating half of the barium chromate is not distinctive and is not accurate for rapid analysis. The precipitation cannot be controlled by reduction of half the chromate because a brown precipitate, probably hydrated chromium dioxide, is formed as the solution is neutralized, and practically no barium chromate is precipitated. Lead chromate was observed to be only slightly soluble in dilute nitric acid. Half of the chromate may be easily removed by precipitation with lead. However, the lead chromate carries a small amount of radium chromate, and this loss would be additive.

The timed reaction depends upon the rate of hydrolysis of urea in a hot solution. If boiling nitric acid (1 molar) is saturated with barium chromate, diluted with three parts of water, and, after the addition of urea (60 grams per liter of solution), heated to 100° and maintained at this temperature for 42 minutes, then approximately 50 per cent of the dissolved barium chromate precipitates. For each minute over 42 minutes an additional 3 per cent of the barium chromate is precipitated. For example,

under carefully controlled conditions, 59 per cent of the dissolved barium chromate was precipitated in 45 minutes. This study indicates that rather close timing is required.

A series of fractional chromate precipitations were carried out based upon the fact that 50 per cent of the barium chromate will carry 95 per cent of the radium chromate. Theoretically seven fractionation steps should be required for a hundred-fold enrichment. The following experiment was a test of this theory. The original sample was a barium-radium carbonate mixture (Ba:Ra = 96,930:1) purified from K-65 residues.

Procedure

Reaction 1 - One hundred grams of a barium-radium carbonate mixture is moistened with 250 milliliters of water and dissolved by slowly adding 100 milliliters of concentrated nitric acid. After diluting with water to 3,000 milliliters, the nitrate solution is heated to 95°. Fifty grams of potassium chromate, dissolved in 200 milliliters of hot nitric acid (1:3), is added slowly with stirring followed by the addition of 192 grams of solid urea. After dissolution of the urea the solution is maintained at 100° until sufficient urea hydrolyzes to raise the pH of the solution to 5. The barium chromate (Precipitate 1) is filtered. The filtrate (Filtrate 1) is saved and used in Reaction 8. No time control is necessary for Reaction 1 since enough potassium chromate is added to precipitate only 50 per cent of the dissolved barium.

Reactions 2-7 - The precipitate from the preceding reaction is dissolved in hot, 1-molar nitric acid and diluted with hot water. After

the addition of urea, the temperature is maintained at 100° for 42 minutes. The reaction is stopped by the addition of a few milliliters of cold water to cool the solution below 90°. The chromate precipitate is filtered immediately. The filtrate is reheated and maintained at 100° until the pH is 5. The mixture is allowed to cool, and the chromate is filtered. The final filtrate from this second crop of chromate crystals is essentially free of radium and barium and is discarded. The quantities of materials used and the numbers assigned the fractions for Reactions 2 through 7 are shown in Table I.

Reaction 8 - The chromates from Filtrates 2 and 3 and 3.0 grams of potassium chromate are dissolved in 600 milliliters of hot, 1-molar nitric acid and added to Filtrate 1, which has previously been heated to 95°. Since Filtrate 1 already contains urea and since Reaction 8 is not time-controlled, no additional urea is required. The temperature of the solution is maintained at 100° until the pH is 5. The mixture is allowed to cool, and the chromate (Precipitate 8) is filtered. The remaining alkaline earth in the filtrate is recovered as carbonate (Filtrate 8) by the addition of an excess of sodium carbonate solution.

Reaction 9 - The chromates from Filtrates 4, 5, 6 and 7 and Precipitate 8 are dissolved in 715 milliliters of hot, 1-molar nitric acid and diluted with 2,145 milliliters of hot water. After the addition of 172 grams of urea, the temperature is maintained at 100° for 42 minutes. The reaction is stopped by the addition of a few milliliters of cold water to cool the solution below 90°. The chromate (Precipitate 9) is filtered

immediately. The filtrate is reheated and maintained at 100° until the pH is 5. The mixture is allowed to cool and the chromate (Filtrate 9) is filtered.

Results and Discussion

Each precipitate and filtrate from the above 9 reactions were analyzed for both barium and radium by the methods described in the previous Quarterly Report.¹ The results of these analyses along with barium to radium ratios are listed in Table II. The distribution of the original barium and radium between the various fractions is shown in Table III. All but four fractions, Precipitate 7, Precipitate 9, Filtrate 8, and Filtrate 9, were reworked. Precipitate 7, the radium fraction, was composed of 1.0 per cent of the original barium and 67.2 per cent of the original radium (Ba:Ra = 1,500:1). Precipitate 9 was of similar composition as the original sample and may be reworked. The carbonate from Filtrate 8 and the chromate from Filtrate 9 are waste fractions. The analysis of these final fractions is found in Table IV. The summation of the barium and radium in these final fractions is in excellent agreement with the original amounts of barium and radium indicating a good material balance.

The fractional precipitation series is shown schematically in Figure 1. Partition factors, D , are shown on the figure along with the per cent of the original barium and radium in each fraction and its barium to radium ratio. For comparison a theoretical series based upon 50 per cent precipitation of the barium chromate carrying 95 per cent of the radium chromate ($D = 19$) is shown in Figure 2. The agreement between the two is good.

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The results obtained by the above experiment indicates that the chromate-urea method is rapid and gives good recovery of the radium. Experiments are in progress for the final purification of radium using the 1500:1 material obtained from Reaction 7 as the starting sample.

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Table I
MATERIAL FOR REACTIONS 2-7

	<u>Reaction</u>					
<u>Material</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Precipitate Employed (No.)	1	2	3	4	5	6
1 Molar HNO ₃ (ml.)	800	400	200	100	50	25
Hot Water (ml.)	2400	1200	600	300	150	75
Urea Added (Grams)	192	96	48	24	12	6
Precipitate Produced (No.)	2	3	4	5	6	7
Filtrate* Produced (No.)	2	3	4	5	6	7

* "Filtrate" refers to the solid chromate obtained from the filtrate of the time-controlled precipitation.

Table II
ANALYSES OF CHROMATE-UREA FRACTIONS

<u>Reaction</u>	<u>Ba (Grams)</u>		<u>Ra (Microcuries)</u>		<u>Ba:Ra</u>	
	<u>Precipitate</u>	<u>Filtrate</u>	<u>Precipitate</u>	<u>Filtrate</u>	<u>Precipitate</u>	<u>Filtrate</u>
Original	67.92	--	700.7	--	96,930:1	--
1	35.62	32.30	648.9	29.2	54,960:1	1,106,000:1
2	17.07	18.00	601.9	35.9	28,380:1	501,400:1
3	8.72	8.13	581.6	26.8	14,990:1	303,900:1
4	4.72	3.90	519.4	19.0	8,763:1	205,300:1
5	2.28	2.37	522.3	30.8	4,373:1	77,050:1
6	1.19	1.07	480.9	28.1	2,470:1	38,040:1
7	0.71	0.45	471.2	17.3	1,500:1	26,160:1
8	29.76	29.31	114.4	21.4	260,100:1	1,370,000:1
9	15.42	20.86	183.8	21.9	83,900:1	952,500:1

Table III

DISTRIBUTION OF THE ORIGINAL BARIUM AND RADIUM BETWEEN THE VARIOUS FRACTIONS

<u>Reaction</u>	<u>% Original Barium</u>		<u>% Original Radium</u>	
	<u>Precipitate</u>	<u>Filtrate</u>	<u>Precipitate</u>	<u>Filtrate</u>
1	52.4	47.6	92.5	4.2
2	25.1	26.5	85.9	5.1
3	12.8	12.0	83.0	3.8
4	6.9	5.7	74.1	2.7
5	3.4	3.5	74.5	4.4
6	1.8	1.6	68.6	4.0
7	1.0	0.7	67.2	2.5
8	43.8	43.2	16.3	3.1
9	22.7	30.7	26.2	3.1

Table IVANALYSES OF THE FINAL CHROMATE-UREA FRACTIONS

<u>Final Fractions</u>	<u>Ba (Grams)</u>	<u>Ra (Microcuries)</u>
Precipitate 7	0.71	471.2
Precipitate 9	15.42	183.8
Filtrate 8	29.31	21.4
Filtrate 9	<u>20.86</u>	<u>21.9</u>
Total	<u>66.30</u>	<u>698.3</u>
Original	67.92	700.7

FIGURE 1

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EXPERIMENTAL FRACTIONAL CHROMATE PRECIPITATIONS
 BASED ON 50 % OF THE BARIUM CHROMATE CARRYING
 95 % OF THE RADIUM CHROMATE

FIGURE 2

MEM-498

THEORETICAL FRACTIONAL CHROMATE PRECIPITATIONS
BASED ON 50% OF THE BARIUM CHROMATE
CARRYING 95% OF THE RADIUM CHROMATE

MLM-498
Problem Title - The Absorption of Barium on Dowex 50 from Acid Chromate Solution

Report By - G. D. Nelson

Work Done By - G. D. Nelson

INTRODUCTION

In the proposed scheme of radium purification the radium-barium mixture is received as the chromate. The separation of the chromium from the desired radium would be simplified if an acid solution of the chromates could be used to place the active mixture at the top of an ion exchange column (for subsequent barium removal) and at the same time remove the chromium. This plan was thought possible since Dowex 50 is a cation exchange resin and the chromate ion is negatively charged. The problem as studied here has two aspects, namely, complete absorption of barium ions by the resin at the top of the ion exchange column and complete separation of the chromium from the barium.

DETAILED REPORT

Preparation of Ion Exchange Column

Dowex 50 (or Nalcite HCR, high capacity resin) cation exchange resin was used for this work. Table I gives some of the characteristics of this material.¹ The weighed, air-dried resin was put in a glass tube of approximately one square centimeter cross-sectional area with suitable Tygon tubing connections to remove air, permit backwash, admit solutions, etc. Before treatment with the chromate solution the resin in the column was "conditioned" by the following cycle, a modification of the Boyd procedure.²

1. Backwash the column with distilled water to remove the finely-divided resin particles (fines). About 0.1 per cent of the resin is removed in this manner, and most of the fines pass through 100-mesh screen.

2. Convert sodium resin to acid form by treatment with sufficient 10 per cent hydrochloric acid solution.

3. Wash with water to remove chloride ion.

4. Convert resin to the sodium form by contact with a solution of 10 per cent sodium chloride with sodium ion content equal to two times the capacity of the resin.

5. Wash with water to remove excess chloride ion.

After this conditioning treatment, which removes contaminating ions from the resin, the column is ready to exchange its sodium ions for other cations most efficiently.

Barium Absorption by Sodium Dowex 50

Dried barium chromate equal in weight to one-tenth the chemical equivalent of the resin present was dissolved in one milliliter of concentrated nitric acid and 150 milliliters of water. The pH was measured, and the solution was then passed through the column at a rate of approximately 1 to 1.5 milliliters per minute per square centimeter of cross section. This solution was followed by 150 milliliters of water to rid the column of chromate ion. When this step was accomplished, the solution coming from the column was colorless. The chromate solution from the column and the wash water were combined and analyzed for chromium by an iodimetric method. No barium was found in this chromate solution.

Barium Citrate Precipitation

In order to locate the barium on the column, the resin was treated with sufficient 10 per cent ammonium citrate solution at a rate sufficiently slow to give a precipitate of barium citrate where the barium was located on the column.

In Figure 1, A indicates the top of the column, and B the point at which the resin containing barium meets the resin which contains no barium. As was predicted, this was the top one-tenth of the column as indicated by the barium citrate in the spaces between the resin granules between A and B in the figure. (The fact that barium citrate may precipitate is objectionable as far as the proposed process for radium purification is concerned, but the above technique for locating the position of the barium on the resin column is of some interest.)

Removal of Barium from the Column for Analysis

A stripping method was selected to recover the barium from the column. Stripping has two advantages over ashing the resin for barium recovery: It simulates process practice and is non-destructive, i.e., the resin is left in a form (ammonium resin) for any succeeding barium chromate treatment. An ammonium hydroxide (15 per cent), ammonium citrate (10 per cent) solution was used to dissolve and remove the precipitated barium citrate from the column. A volume of 100 or 150 milliliters of the stripping solution was passed through the column at a rate of 1.5 milliliters

per minute. This solution was followed by a wash of 100 to 150 milliliters of water to remove any citrate from the column and any barium from the transfer lines. This solution was analyzed for barium by precipitating the barium as the chromate and titrating the chromate by the iodimetric method.

Results of four runs made with two different columns are given in Table II. The data indicate:

1. Complete separation of chromate ion from the barium.
2. Quantitative absorption of the barium at the head of the resin column in a suitable position for subsequent elution to remove the barium.
3. Complete recovery of the barium by removal with an ammoniacal citrate solution. The limit of titration error in the analyses is equal to ± 0.3 per cent of the total. It is felt that disparity in the results of the earlier runs (1 and 2) is caused by poor technique.

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Table I
CHARACTERISTICS OF THE SODIUM FORM OF DOWEX 50

<u>Size of Granules Retained on U.S.</u>	<u>Per Cent</u>
18 Mesh	0.49
30 Mesh	61.15
45 Mesh	32.00
60 Mesh	4.57
70 Mesh	0.91
100 Mesh	0.80
100 Mesh	<u>0.08</u>
Total	100.00
Per Cent Moisture (by air drying)	39.7
Per Cent Moisture (by oven drying)	48.2
Grams Per Equivalent (oven dried resin)	225

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Table IIABSORPTION OF BARIUM ON DOWEX 50 FROM ACID CHROMATE SOLUTION

<u>Run No.</u>	<u>Weight of Resin Oven Dried (grams)</u>	<u>Barium Chromate Feed Solution</u>			<u>Stripping Solution Recovery</u>			
		<u>Wt. BaCrO₄ Per 150 ml. H₂O (grams)</u>	<u>pH of Feed Solution</u>	<u>Flow Rate (ml./min.)</u>	<u>Flow Rate (ml./min.)</u>	<u>Volume (ml.)</u>	<u>Chromate (Per Cent)</u>	<u>Barium (Per Cent)</u>
1	13.85	0.7798	1.18	--	--	100	--	99.3
2	14.06	0.7920	1.23	1.2	1.43	100	98.3	99.3
3*	13.85	0.7798	1.20	1.48	1.50	150	98.8	100.0
4	14.06	0.7920	1.33	1.15	1.37	150	99.3	100.0

* Picture made of precipitated barium citrate on column during Run 3.

DOWEX-50 CONTAINING BARIUM CITRATE

Problem Title - Separation of Radium and Barium by Ion Exchange
Report By - W. C. McCluggage
Work Done By - W. C. McCluggage and M. F. Hauenstein

INTRODUCTION

Tompkins¹ method for radium-barium separation is being studied further to determine its applicability for radium production.

Because of the possibility of receiving the enriched barium-radium in the ratio of approximately 2,000:1 from fractional chromate precipitation,² the work has been directed mainly toward completing the separation by the ion exchange method of Tompkins.

In the first of two runs the barium was eluted with 10 per cent citric acid at pH 5, and the radium was eluted with six normal nitric acid. In the second run both elements were eluted with 10 per cent citric acid of pH 5 in order to calculate the distribution coefficients, separation factor, and the number of theoretical plates as described by S. W. Mayer and E. R. Tompkins.³

DETAILED REPORT

Analytical Methods

Radium was determined by the alpha counting method of Tompkins and co-workers.⁴ This method is applicable in cases that involve no appreciable solids on the slides. Since the samples contained little or no barium, no correction for self absorption was needed.

It is possible to obtain radium analyses by direct sampling of effluent that check favorably with results obtained by the Tompkins method. A slide is prepared from the fresh effluent, dried, ignited, then allowed to stand two hours before counting. Some fractions from the second separation were analysed by both methods, and the results are given in Table V.

Two methods of barium analysis were used. The very dilute fractions were analysed turbidometrically. The more concentrated fractions were determined volumetrically. The barium was precipitated as the chromate which was retained on a filter disc, washed, dissolved in five normal hydrochloric acid, excess potassium iodide added, and the liberated iodine titrated with standard thiosulfate solution.

Column Separations

Two column separations in which the barium-radium ratio was approximately 2,000 to 1 were made. The data and operating conditions for this work are given in Tables I and V and Figures 1 and 2. In both separations material balance was obtained for radium but in each case the barium return was high.

The first elution was started with 20 per cent citric acid, pH 5, instead of the required 10 per cent. Since about 60 milliliters passed the column before the change was made, the effect was to displace the barium and radium band downward an unknown distance, thus giving a shorter bed depth than was indicated.

The barium elution was complete after the passage of 250 milliliters of the citrate solution, 60 of which was 20 per cent. After the

[REDACTED]

passage of 250 milliliters of water which displaced the remaining citrate solution, 43 per cent of the radium had left the column in the citrate or citrate-water fractions. Over half of this radium contained detectable quantities of barium. The water treatment was followed by 150 milliliters of six normal nitric acid which removed the remaining 57 per cent of the radium. Elution of radium by nitric acid eliminates the necessity of recovering the radium from the citrate solution since evaporation may be used. A slightly longer column should separate the two elements sufficiently to permit 90 per cent or more of the radium to be eluted with nitric acid.

In the second run, 10 per cent citric acid at pH 5 was used for the entire elution. The data for this separation are given in Table II and Figure 2.

Traces of barium were detected in the 18th fraction and very little radium was found in fractions below 22. It is probable that barium disappears completely from the system in the 20th or 21st fraction. (At this point the column could be washed free of citrates and the radium eluted with six normal nitric acid which would remove 98 per cent of the radium as the nitrate.) Ammonium ion would be present as a result of the resin being converted to the hydrogen form.

Calculation of Column Separation Efficiency

Mayer and Tompkins⁴ have developed the following expression for the separation efficiency of an ion exchange column by assigning to it a number of theoretical plates similar to the concept of expressing efficiency of fractional distillation.

[REDACTED]

$$p = 2 \pi C (C + 1) (L \max p)^2$$

where p is the number of theoretical plates in the column, $(L \max p)$ is the fraction of the total solute in the column volume of elutrient containing the maximum concentration of that solute, (0.256 for barium) and C is the solute distribution coefficient between the solution and resin in a given column volume. Mayer and Tompkins show that the distribution coefficient, C , is equal numerically to the number of the column volume in which the maximum fraction of the solute is present (10 for barium). The number of theoretical plates for barium from the data of Figure 2 is calculated to be 45 and the number for radium, 136. It is probable that the column has more theoretical plates for radium than for barium because of the much greater concentration of the latter and the slower rate at which a more concentrated solution passing a resin section can reach equilibrium with the resin. That the dilute radium solutions are in closer equilibrium with the resin than the more concentrated barium solutions is illustrated by the symmetrical shape of the radium elution curve of Figure 2 and the unsymmetrical shape of the barium curve.

The separation factor for radium and barium, equivalent to the ratio of their distribution coefficients is 29/10 or 2.9.

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3. Mayer, S. W. and Tompkins, E. R., J. Am. Chem. Soc. 69, 2866-2874 (1947).

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Table IELUTION OF BARIUM AND RADIUM - FIRST RUN

<u>Fraction Number</u>	<u>Barium Content Per Fraction (Micrograms)</u>	<u>Per Cent of Total Barium</u>	<u>Radium Content Per Fraction (Micrograms)</u>	<u>Per Cent of Total Radium</u>
1				
2				
3	15,400	9.6		
4	107,100	67.0		
5	28,900	18.0	0.27	0.44
6	7,700	4.8	0.88	1.42
7	1,000	0.6	2.46	3.97
8			5.48	8.85
9			10.65	17.2
10			6.85	11.0
11			0.87	1.40
12			5.77	9.30
13			29.00	46.8
14			0.47	0.76
15			0.04	0.06

Table IIELUTION OF BARIUM AND RADIUM - SECOND RUN

<u>Column Volume</u>	<u>Barium Content Per Fraction (Micrograms)</u>	<u>Per Cent of Total Barium</u>	<u>Radium Content Per Fraction (Micrograms)</u>	<u>Per Cent of Total Radium</u>
1 & 2				
3				
4				
5				
6				
7				
8	7,980	5.85		
9	27,260	20.00		
10	34,800	25.60		
11	31,870	23.40		
12	21,220	15.62		
13	10,940	8.05		
14	8,470	6.23		
15	3,640	2.68		
16	1,935	1.42		
17				
18				
19			0.05	
20			0.13	
21			0.31	
22			0.49	
23			1.26	1.98
24			3.02	4.77
25			4.12	6.50
26			6.25	9.85
27			8.36	13.18
28			9.99	15.71
29			10.00	15.73
30			8.10	12.75
31			5.86	9.25
32			3.46	5.45
33			1.78	2.80
34			0.69	1.09
35			0.32	0.55
36			0.08	

Table III
OPERATION STEPS FOR FIRST RUN

<u>Process Steps</u>	<u>Reagents Used</u>	<u>Volume</u>	<u>Cation Return</u>	
			<u>Barium</u>	<u>Radium</u>
Feed Solution	0.124 g. Ba as Chromate 62.0 μ g. Ra 0.2 N HNO ₃	270 ml.		
Ba Elution	10% Citric Acid pH 5	200 ml.	0.165 g.	26.6 μ g.
Ra Elution	6N Nitric Acid	150 ml.		35.4 μ g.

Table IV
OPERATION STEPS FOR SECOND RUN

<u>Process Steps</u>	<u>Reagents Used</u>	<u>Volume</u>	<u>Cation Return</u>	
			<u>Barium</u>	<u>Radium</u>
Feed Solution	0.136 g. Ba as Chromate 63.5 μ g. Ra 0.2 N HNO ₃	1500 ml.		
Ba Elution	10% Citric Acid pH 5	330 ml.		0.149 g.
Ra Elution	10% Citric Acid pH 5	265 ml.		65.0 μ g.

Table VCOMPARISON OF RADIUM ANALYSES BY THE AERATION AND DIRECT METHODS

<u>Fraction Number</u>	<u>c./min./vol. Aeration</u>	<u>c./min./vol. Direct</u>
23	2.79×10^6	
24	3.34×10^6	3.26×10^6
25	4.54×10^6	4.64×10^6
26	6.92×10^6	6.94×10^6
27	9.22×10^6	9.50×10^6
28	1.10×10^7	1.079×10^7
29	1.10×10^7	1.090×10^7

Table VI
PHYSICAL DATA FOR COLUMN 4 AND 5

<u>Item</u>	<u>Separation 1</u>	<u>Separation 2</u>
Resin	Dowex 50; NH ₄ R 70-100 Mesh	Dowex 50; NH ₄ R 70-100 Mesh
Bed Depth	20 cm.	25 cm.
Bed Diameter	13 mm.	13 mm.
Wt. of Resin (Oven Dried)	13.0 gm.	16.3 gm.
Bed Volume	26.6 ml.	33.2 ml.
*Column Volume	13.3 ml.	16.6 ml.
Liquid Above Resin	10 cm. 10% NaCl	10 cm. H ₂ O
Drop Rate of Feed	1 ml./min./cm. ² ± 0.2 ml.	1 ml./min./cm. ² ± 0.1 ml.
Drop Rate of Elutrient	0.3 ml./min./cm. ² ± 0.05 ml.	0.3 ml./min./cm. ² ± 0.03 ml.

* Column volume based on the amount of solution required to wet the resin and fill the voids between particles of the air-dried bed.

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ELUTION CURVE FOR FIRST SEPARATION OF RADIUM AND BARIUM.

FIGURE 1

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ELUTION CURVE FOR SECOND SEPARATION OF RADIUM AND BARIUM.

FIGURE 2

MCM-498

Problem Title - The Decontamination of Liquid Wastes from the Radium Process

Report By - R. W. Moshier

Work Done By - R. W. Moshier

INTRODUCTION

Decontamination studies were continued during this quarter in order to find a satisfactory method which would bring the count on the waste solutions from the Radium Process to a sufficiently low level for discharge into natural waters. This method has been developed.

A new waste liquor has been added (the filtrate from chromate fractionation) and two waste liquors have been eliminated (the water leach and the hydrofluoric-sulfuric acid filtrate) as a result of changes in the bench-scale process.

DETAILED REPORT

The recommended procedure for decontamination of liquid wastes for Radium Process is as follows:

1. The three wastes, (a) chromate fractionation filtrate, (b) sulfate precipitation filtrate, and (c) the sodium carbonate filtrate are mixed together.

2. The mixture is acidified by the addition of concentrated sulfuric acid at such a rate that the carbon dioxide evolution does not cause overflow of the containing vessel. After a pH of 2 has been reached and at which time the carbon dioxide is no longer being evolved, the solution is stirred rapidly.

[REDACTED] 198

3. Excess sulfuric acid is added in sufficient quantity to neutralize the sodium hydroxide leach used in the next step, and the solution is thoroughly mixed.

4. As much sodium hydroxide leach as is available, preferably a volume equal to that obtained in Step 3, is placed in a separate reaction vessel. This liquor is neutralized with the acid mixture from Step 3 to pH 8 as determined with alkacid paper. Neutralization results in a thick slurry. The precipitate consists principally of lead compounds and acts as a carrier for nearly all of the radioactive elements present.

5. The slurry then is allowed to settle, preferably overnight, in order to facilitate more rapid filtration by decantation before the bulk of the precipitate is placed upon the filter. Filtration on a Buchner funnel through Whatman No. 1 filter paper with suction is more rapid than gravity filtration. As the filter cake becomes drier and cracks form, the filter cake is homogenized by manipulation with a spatula, to permit removal of more of the liquid from the cake.

6. One milliliter of 0.1 molar potassium ferrocyanide is now added to the filtrate for each 100 milliliters of liquid and mixed. Two milliliters of 0.1 molar ferrous solution is added (ferrous ammonium sulfate solution was used). The solution is mixed, allowed to settle, preferably overnight, and filtered. Since the precipitate is small and gelatinous, it is filtered on a bed of diatomaceous earth or equivalent filter-aid. Crystal clear filtrates have less than half the residual count of that of slightly turbid filtrates.

[REDACTED]

7. Alpha counts are made on 500-lambda samples mounted on 2-inch glass discs with the parallel plate alpha counter of 50 per cent geometry, and the alpha plus beta counts on the Nuclear Measurements Corporation PC-1 windowless chamber counter with a 50 per cent geometry.

Some sample runs were made as follows:

First Step - Neutralization of Mixed Wastes

In a 4-liter beaker 470 milliliters of the chromate fractionation filtrate, 530 milliliters of the sulfate filtrate, and 1,000 milliliters of sodium carbonate filtrate were mixed. Sixty milliliters of concentrated sulfuric acid brought the pH of this mixture to pH 2. Stirring was accomplished with a magnetic stirring bar. The sulfuric acid was added from a buret with the tip immersed. Then 153 milliliters of additional acid was added.

A volume of 1,800 milliliters of sodium hydroxide leach was placed in another 4-liter beaker containing a magnetic stirring bar. The preceding acidified solution was fairly rapidly added to a final pH of 8. After standing overnight, the supernatant was decanted into a large Buchner funnel fitted with a Whatman No. 1 filter paper. Finally, the settled slurry was also added to the funnel and the beaker rinsed with a little water. When the filter cake cracked, it was manipulated with a spatula until no more filtrate could be sucked off.

Second Step - Ferrous Ferrocyanide Scavenging

A solution of 40 milliliters of a tenth molar potassium ferrocyanide was added to the filtrate in a 4-liter beaker obtained from Step 1 which corresponds to 1 milliliter of reagent per 100 milliliters of solution. After mixing with a magnetic stirrer, 80 milliliters of a tenth

molar ferrous ammonium sulfate solution was added which caused an amorphous precipitate to form. The mixture was allowed to settle overnight and filtered on a Buchner funnel with Whatman No. 42 paper precoated with a one-eighth inch bed of diatomaceous earth.

A second run was made on a mixture containing 400 milliliters of chromate-fractionation filtrate, 500 milliliters of sulfate filtrate, 100 milliliters of unknown mixed waste, 1,000 milliliters of sodium carbonate filtrate, and 315 milliliters of concentrated sulfuric acid. This mixture was added to 1,800 milliliters of sodium hydroxide leach producing a pH of 8. The remaining steps were the same as in the first example. The results of the two runs are shown in Table I.

The results of various methods of decontamination which were tried on different types of waste solutions are shown in Tables II, III, and IV. The sodium carbonate filtrate (Table II) showed the best decontamination by essentially the same procedure as previously described. The results are poorer and less consistent probably because sufficient lead is not present to act as a carrier. The chromate filtrate (Table III) showed poor decontamination unless neutralized with the filtrate from the sodium hydroxide leach which contained lead to act as a carrier. In these experiments the ferrous ferrocyanide precipitation gave little additional decontamination. The sodium hydroxide leach (Table III) is readily decontaminated by the standard procedure. However, it is better to take advantage of the decontaminating ability of its lead content by mixing with other waste solutions before precipitating the lead.

The information on the various waste solutions is summarized in Tables V and VI.

CONCLUSION

A two-step process has been developed for decontamination of bench-scale radium-process wastes. Effluent liquor obtained from this process are within the limits 10 to 30 counts per minute per milliliter. Some 60 liters of wastes have been decontaminated. The dried residues containing the activity amount to 0.033 grams per milliliter of waste solution.

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Table I

SUMMARY OF RESULTS FROM TWO EXAMPLES OF
DECONTAMINATION BY THE RECOMMENDED PROCEDURE

<u>Example</u>	<u>Wet Filter Cake 1st Step</u>		<u>Air Dried 25° Filter Cake</u>		<u>Original Count Estimated Composite c./min./ml.</u>		<u>Count After 1st Step c./min./ml.</u>		<u>Count After 2nd Step c./min./ml.</u>	
	<u>Total g.</u>	<u>g./ml.</u>	<u>Total g.</u>	<u>g./ml.</u>	<u>Alpha</u>	<u>Beta</u>	<u>Alpha</u>	<u>Beta</u>	<u>Alpha</u>	<u>Beta</u>
1	330.5	0.083	120.0	0.030	5,238	14,108	8	64	4	10
2	323.5	0.081	145.0	0.036	8,882	14,564	14	66	16	18

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Table II
SODIUM CARBONATE FILTRATE DECONTAMINATION

<u>Experiment Number</u>	<u>Treatment</u>	<u>After Treatment c./min./ml.</u>	
		<u>Alpha</u>	<u>Beta</u>
	Original Count	1,425	3,900
1	H ₂ SO ₄ to pH 8 and Filt.	600	2,400
	Ppt. with Na ₂ S	380	1,700
2	H ₂ SO ₄ to pH 8 and Filt.	--	--
	FeS Ppt. with Na ₂ S	80	106
3	H ₂ SO ₄ + NaOH Leach (pH 8)	60	166
	FeS Ppt. with Na ₂ S		148*
	Second FeS Ppt.		96*
4	H ₂ SO ₄ + NaOH Leach (pH 8)**	16	16
	Ppt. Ferrous Ferrocyanide	8	14
5	Repeat of Preceding 2 Steps	0	8
6	Repeat of Preceding 2 Steps	18	82
7	Repeat of Preceding 2 Steps	40	58

* Alpha plus beta count.

** To obtain satisfactory results the sodium carbonate filtrate and the sodium hydroxide leach must be used in approximately equal amounts.

Table IIICHROMATE CRYSTALLIZATION FILTRATE DECONTAMINATION

<u>Counts Per Minute Per Milliliter</u>			
<u>Alpha</u>	<u>Beta</u>	<u>Alpha</u>	<u>Beta</u>
Original Count			
608	756		
<u>After Neut. with NaOH</u>		<u>After Neut. Followed By Ferrous Ferrocyanide</u>	
60	44	68	48
128	142	104	142
110	148	106	114
116	150	140	96
<u>After Neut. with NaOH Leach</u>			
50*			
42	32	36	40
—	—	8	20

* Alpha and beta combined.

Table IVMIXED WASTES AND SODIUM HYDROXIDE LEACH DECONTAMINATION

<u>Test No.</u>	<u>Process</u>	<u>c./min./ml.</u>	
		<u>Alpha</u>	<u>Beta</u>
	Sodium hydroxide leach, original count	480	12,000
1	Sodium hydroxide leach neutralized to pH 8 with concentrated sulfuric acid, filter	0	50
2	Filtrate from No. 1 followed by ferrous sulfide scavage	0	2
3	Miscellaneous high-count filtrates from previous tests, acidified with excess acid and then added to sodium hydroxide leach	6	26
4	Duplicate of No. 3	42	38
5	Filtrate from No. 4 followed by ferrous ferrocyanide scavage	6	8

Table V
TYPICAL ANALYSES OF WASTE SOLUTIONS

	<u>SiO₂</u> <u>g./ml.</u>	<u>PbSO₄</u> <u>g./ml.</u>
Sodium Carbonate Filtrate (15%)	0.001	0.0015
Sodium Hydroxide Leach (10%)	0.043	0.024
Water Soluble* 0.040 g. solids/ml., 0.0056% NO ₃ , 1.5% CO ₂ , 52% SO ₄ , traces of SiO ₂ , CaO, MgO		
HF-H ₂ SO ₄ Filtrate* 0.05 g. solids/ml., 0.0% Pb, 10.4% MoO ₃ , 26.5% Fe ₂ O ₃ , 0.47% Ni 0.0% SiO ₂		
Chromate Crystallization Filtrate	Not analyzed	
Sulfate Filtrate*	Not analyzed	

* Not obtained with the present process.

Table VITYPICAL RADIOACTIVE COUNTS ON LIQUID WASTES FROM RADIUM PROCESS

<u>Type of Waste</u>	<u>Beta Count c./min./ml.</u>	<u>Alpha Count c./min./ml.</u>
Water Soluble*	127	52
Hydrofluoric-Sulfuric* Acid Filtrate	5,400	5,080
Sodium Hydroxide Leach	12,000	480
Sodium Carbonate Filtrate	3,900	1,425
Sulfate Filtrate*	63,000	39,000
Chromate Fractionation	756	608

* Not obtained with the present process.

Problem Title - Radium Analysis of K-65 Residue

Report By - A. W. Martin

Work Done By - A. W. Martin

INTRODUCTION

The radium analysis of K-65 residue in connection with the development of a process for radium separation from this residue consists in the preparation of a proper solution which may be used in alpha counting by the aeration method. The method of Tompkins and co-workers¹ for radium analysis by alpha counting was investigated and is the method which is being used at the present time. In order to have a radium analysis based on this method, the preparation of a proper solution for analysis was devised. The procedure adopted modifies the reported method of Thomas.²

DETAILED REPORT

A solution to be used for the determination of radium by the aeration method should contain no sulfates and no silicates, and the determination is made on samples from which radon can be quantitatively removed. Precipitated silica absorbs radon and makes its quantitative removal difficult. The method used for the preparation of the samples was to remove the bulk of the silica by repeated treatment with hydrogen fluoride (48 per cent solution) and concentrated sulfuric acid. The residue remaining was suspended in water and treated with a large excess (10-fold) of ammonium acetate in order to dissolve most of the lead sulfate. The

precipitate was removed by filtration and washed with ammonium acetate and ammonium sulfate. This precipitate, contained on an ashless filter paper, was ignited, treated with sulfuric acid, and then retreated with hydrogen fluoride (48 per cent solution). The sulfuric acid solution containing barium sulfate was then poured into water. The barium-radium sulfate was filtered on an ashless filter paper, ignited, and then fused with 10 times its weight of sodium carbonate. The resulting melt was extracted with hot water, and the residue of barium-radium carbonate was dissolved in dilute nitric acid. This acid solution was analyzed for radium by the alpha slide aeration method of Tompkins and co-workers.¹

Analysis of four samples, 2.0516, 2.1080, 4.9195, and 4.9896 grams in weight were prepared. Samples of approximately two grams gave discordant results because of small values of alpha counts, however, the approximately five-gram samples gave a value of 344 micrograms of radium per pound of K-65 which is comparable to a value of 335 micrograms of radium per pound of K-65 determined by comparison against a radium standard with gamma counting technique.

REFERENCES

1. 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).
2. Thomas, H. C., Report (1) Radium Analysis, M-2750.

Problem Title - Radium Analysis by Alpha Counting
 Report By - M. F. Hauenstein
 Work Done By - M. F. Hauenstein, W. C. McCluggage, J. B. Otto, and
 W. H. Power

INTRODUCTION

As a fast method of radium analysis by alpha counting, the chloride precipitation procedure, developed by Ames,¹ has been investigated. The procedure was modified for our use. Analysis of Bureau of Standards radium solutions provided data for establishing the amount of self absorption. Solutions containing citrate, chromate, nitrate, and carbonate were analyzed by this method. The citrate solutions also were analyzed by the aeration method.²

DETAILED REPORT

The procedure which we have used is as follows:

1. A one-milliliter sample of the solution to be analyzed is placed in a 15-milliliter centrifuge tube. Ten milligrams of barium as the chloride is added as a carrier.

If there is any barium in the original solution, the amount of carrier added is reduced so that the total amount of barium present is always 10 milligrams since a fixed percentage of the alpha radiation is absorbed by this amount of barium. Any deviation from this quantity of carrier would necessitate a new calibration from standard solutions.

2. The centrifuge tube is placed in an ice bath, and seven milliliters of a cold six to one hydrochloric acid-ether solution is added. The sample is stirred with a platinum wire and then centrifuged for three minutes. The supernatant is removed with a transfer pipette.

3. To the remaining precipitate one milliliter of the hydrochloric acid-ether solution is added. This mixture is stirred, centrifuged, and the supernatant again removed.

4. Repeat Step 3.

5. Conversion from the chloride to the nitrate at this point is necessary to prevent attack of the stainless steel mounting slide. The precipitate in the tube is heated to dryness. Great care must be taken here to prevent spattering. A few drops of nitric acid are added and heated to dryness again.

6. The precipitate is dissolved in a minimum of one normal nitric acid and transferred to a stainless steel slide, two inches in diameter, which has previously been edged with a narrow Zapon band. The tube is washed several times with one normal nitric acid, and the wash solution is placed on the slide.

7. The slide is placed on a hot plate covered with a thin asbestos sheet. A heat lamp is suspended over the hot plate. The slide is heated by both the lamp and the hot plate. When bubbles begin to form, a few drops of one normal sulfuric acid are added to precipitate the sulfate. The deposit is allowed to go to dryness and is then heated over a flame to vaporize any polonium which may have carried through the process.

8. The slide is counted in a parallel plate alpha counter.

Standardization

Fourteen slides were prepared by the above manner from a Bureau of Standards radium solution. This solution contained, per milliliter, 2×10^{-6} milligrams of radium, 40 milligrams of hydrochloric acid, 28 milligrams of perchloric acid, and 0.1 milligram of barium. When the counts obtained are expressed as per cent of known radium present, the results varied from 77.5 per cent to 84.0 per cent with an arithmetic mean of 80.5 per cent. The probable error of a single measurement was ± 1.2 per cent. From these data it was established that only 80.5 per cent of the radium in the standard sample was counted because of absorption or loss of radium.

This same solution was analyzed by the aeration method.² Of six slides prepared, the results, expressed as above, varied from 113 per cent to 145 per cent of known radium present, with an arithmetic mean of 128 per cent and probable error of ± 4 per cent.

Citrate

Three slides were made from a solution containing 10 per cent citrate. The counts obtained were 77.6 per cent, 74.5 per cent, and 77.7 per cent of known radium.

Three slides were prepared from a solution containing 15 per cent citrate. The counts obtained were 78.2 per cent, 82.4 per cent, and 73.7 per cent of known radium.

Three solutions from the ion exchange column were analyzed by both the aeration and chloride precipitation methods. The counts given

in Table I for the chloride precipitation method are those calculated from counts obtained plus absorption factor.

Nitrate

Four slides were prepared from a six normal nitric acid solution. The counts obtained were 76.8 per cent, 79.3 per cent, 81.8 per cent, and 79.7 per cent of known radium.

Chromate

It was not possible to precipitate the radium and barium chlorides in the presence of chromate ion. The chromate ion was reduced by formic acid and the chloride precipitation performed. Four slides gave counts of 67.8 per cent, 76.6 per cent, 74.6 per cent, and 71.8 per cent of known radium. These were lower than was expected and indicated incomplete precipitation. Another batch of four was run, allowing the samples to stand a half hour after the initial addition of the hydrochloric acid-ether solution. The counting results from these slides were 77.5 per cent, 81.5 per cent, 81.5 per cent, and 75.3 per cent of known radium.

Carbonate

Four slides were made from a solution containing carbonate ion. The counts obtained were 75.7 per cent, 78.6 per cent, 79.1 per cent, and 71.3 per cent of known radium.

Summation

Of 31 slides, the results varied from 71.3 per cent to 84.0 per cent of known radium with an arithmetic mean of 79.2 per cent. The probable error of a single measurement is ± 1.66 per cent. The aeration

method does not give as good precision. This poor precision is caused in part by the fact that it involves merely a physical separation of the radium from its daughters where the chloride method is a chemical separation. The chloride method gives a fast analysis, requiring only 60 to 90 minutes. The aeration method requires five to six hours. The aeration method, however, allows many samples to be analyzed simultaneously, whereas the chloride method allows only one sample (three or four slides) to be analyzed each 60 to 90-minute period.

The presence of citrates, nitrates, or carbonates does not interfere with results by the chloride method. Chromates must be reduced to chromic salts before quantitative precipitation of radium chloride can be achieved.

REFERENCES

1. Ames, D. P., et al., Nuclear Energy Series IV-14B, p. 1700 (1949).
2. Power, W. H. and McCluggage, W. C., Radium Analysis Methods, MLM-475, p. 82.

Table I

COMPARISON OF RADIUM COUNTS BY THE AERATION AND CHLORIDE METHODS

<u>Solution No.</u>	<u>Aeration Method (Av. of 3 Counts) c./min.</u>	<u>Chloride Method (Av. of Counts) c./min.</u>
8	6.05×10^6	5.94×10^6
9	1.176×10^7	1.085×10^7
10	7.566×10^6	6.65×10^6

Problem Title - Radon Counting with the Proportional Counting Chamber
Report By - W. H. Power
Work Done By - W. S. Stringham

INTRODUCTION

Radon counting is a sensitive method of analyzing for radium in amounts of 10^{-9} grams or less. The alpha slide techniques for radium have their lower limit at 10^{-9} grams for reasons of background, absorption, and daughter activity variation. Initial runs with the radon proportional counter were not satisfactory because of difficulties encountered in obtaining reproducible analyses.^{1,2}

DETAILED REPORT

Inconsistent results obtained with the proportional counter apparatus for radon analysis were believed to be caused by (1) leakage of trace quantities of oxygen, water vapor, nitrogen, or other contaminants into the proportional counting chamber along with the radon and P10 gas, causing a shifting of the voltage plateau and damping of the counting rate and (2) incomplete transfer of radon to the counting chamber. The radon collection and transfer apparatus was modified with several suggestions of Fineman³ for reducing the volume and eliminating dead-end parts of the apparatus which might trap radon but which could not be washed out with P10 gas.

Modifications of the radon collection apparatus previously described¹ include the use of a capillary mercury manometer with a one

millimeter bore to reduce dead-end volume (Figure 1, Point A). A copper turning tube, heated to 435° , was inserted at Point B to remove traces of oxygen; a Pirani gauge was added to test for leaks in the apparatus; a second dry ice trap composed of a spirally wound copper coil immersed in a dry ice-trichloroethylene bath was placed at Point B; and a small Bourdon gauge was inserted at Point E. A needle valve was placed at the entrance to the proportional counting chamber to eliminate back diffusion of radon after filling the chamber. All "Y" connections were changed to three-way stopcocks to eliminate dead gas pockets. Apiezon grease was used on all stopcocks or ground glass joints.

The de-emanation step was modified to minimize any leakage of air into the de-emanated radium sample during the radon growth period. The aqueous solution of radium was refluxed for one-half hour with P10 gas slowly bubbling through the solution. After the refluxing, the large stopcock, G, was closed, but pressure of P10 was continued at H until the flask and contents were cooled to room temperature with tap water. After room temperature was reached, Stopcock H was closed. The radon generator was closed under positive P10 pressure by this procedure instead of being under negative pressure which would be caused by closing both stopcocks while the flask was hot and then allowing the flask to cool to room temperature.

After the radon growth period, the apparatus was assembled as indicated by Figure 1, and Points J and K opened to the Welsh vacuum pump. The system was connected to the Pirani gauge at C, and pumping was

continued until a pressure in the range of 0.1 millimeter of mercury was attained. Cock K was closed to the pump, and Cock J was closed to both the pump and system. Cock G was carefully opened until the mercury manometer slowly fell. When the mercury level was constant, Cock J was cracked to connect the radon generator to the line leading to the counting chamber. The radium solution was heated to boiling and allowed to reflux for 15 to 20 minutes while bubbling P10 gas into the solution. About 25 minutes was required for the pressure inside of the manifold to reach atmospheric pressure, after which the needle valve just outside of the counting chamber was closed to avoid possible back diffusion. The radon was allowed to stand in the counting chamber for approximately 10 minutes before a count was taken. Several 10-minute counts were taken at a chamber voltage of 1,250 volts until consistent counting rates were realized (after correction for decay of radon and growth of its daughters).

To check for leakage of air into the system, the copper turnings in the oxygen trap were completely reduced with hydrogen gas before each run. Any tarnishing of the copper during a run showed the presence of oxygen in the system, and low counting rates were realized for the Bureau of Standards radium samples. When unknown samples are run, therefore, results should be discarded if copper tarnishing is noted.

Two runs with good radon recovery efficiencies were made. In each case, all of the above precautions were taken, and absence of copper tarnishing proved that traces of air had not entered the radon generator or transfer system. Recoveries of 84 per cent for a 10^{-9} gram radium

source and 87 per cent for a 10^{-8} gram radium source were obtained. Detailed data are listed in Table I.

It is believed that consistent results with good yields of radon recovery can be realized when the proportional counting apparatus is used if adequate precautions are taken to assure a tight system and to eliminate traces of air. Such precautions, however, limit the capacity of the apparatus to about two runs a day which would be inadequate for control purposes. An ionization chamber counting system which is less sensitive to traces of air, described by Fineman,³ is being constructed to provide for a greater number of radon analyses per day.

Use of Activated Carbon as a Radon Adsorber

A scheme to eliminate deleterious effects of air in the proportional counting system and to allow unlimited quantities of P10 flushing gas to be used to sweep radon from the radium solution involved the adsorption of radon in an activated carbon trap. The trap (Part L, Figure 1) was inserted in the transfer system at Point F. One gram of Columbia activated carbon, No. 6-G, 8 to 14 mesh, was placed in the trap, and the trap was immersed in a dry ice-trichloroethylene mixture. Gas from the radon generator was allowed to pass to the counting chamber as described above. No increase of counting rate over background was noticed when flushing 10^{-8} and 10^{-9} gram radium samples, which indicated that practically complete adsorption of radon was realized in the activated carbon. The carbon trap, still immersed in its dry ice bath, was transferred to ball and socket joint, M, just before the entrance to the counting chamber to make the ratio of

chamber volume to transfer system volume a maximum. The dry ice bath was taken from the carbon trap, and the carbon was heated to redness with a Bunsen flame to drive off radon as completely as possible as P10 gas flowed through the trap to the counting chamber.

Efficiencies of 87 per cent and 70 per cent for radon from 10^{-9} and 10^{-8} grams of radium were obtained, which showed that most of the radon is released by the carbon by heating to redness. With sufficient work to establish a refined technique it is probable that consistent results for radon evaluation can be obtained by adsorption by cooled, activated carbon and transfer by heating to a proportional counting chamber. The lengthy procedure involved, however, would again limit the number of runs to one or two per day and would offer no advantage over the regular method. It is possible that this procedure would be applicable for low level counting of air or breath samples where increased counting rates would be obtained by passing large volumes of the air through cooled carbon.

REFERENCES

1. Power, W. H., Quarterly Report for General Research, MLM-443-2, pp. 34-38.
2. Power, W. H. and McCluggage, W. C. Report for General Research, MLM-475, pp. 82-99.
3. Fineman, P., et al., National Nuclear Energy Series IV-14B, p. 1206 (1949).

FIGURE 1

Table IRADIUM ANALYSES BY THE RADON METHOD WITH THE PROPORTIONAL COUNTER

Run No.	1	2	3*	4*
Grams of Radium in Solution (Bureau of Standards)	10 ⁻⁹	10 ⁻⁸	10 ⁻⁹	10 ⁻⁸
Radon Growth Time (Hours)	22.8	24	102	21.2
Per Cent Equilibrium of Radon with Radium	15.8	16.3	70.8	14.6
Vacuum in mm. Hg	0.15	0.075	--	0.2
Transfer Time (Minutes)	22	32	15	19
Copper Tarnishing (Oxygen Present)	None	None	--	None
Background (Counts per Min.)	58	102	76	34
Radon Decay Time (Minutes)	60	96	32	87
Counts per Min./Microcurie of Radon	3.85 x 10 ⁶	4.13 x 10 ⁶	3.55 x 10 ⁶	4.07 x 10 ⁶
Counts per Min. for Sample	512	5820	2190	4120
Grams of Radium by Analysis	0.84 x 10 ⁻⁹	0.87 x 10 ⁻⁸	0.87 x 10 ⁻⁹	0.70 x 10 ⁻⁸
Per Cent of Bureau of Standards Value	84	87	87	40

* Radon adsorbed on carbon before transfer to proportional counting chamber.

Problem Title - Chemical Engineering Development of the Radium Process

Report By - H. L. Rawlings

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

INTRODUCTION

During the first half of this quarter work progressed on the design of a pilot plant for the Radium Process. This work was chiefly concerned with completing a flow sheet for the residue treatment portion of the process, preparing new cost estimates for Area 1-C of the proposed Semi-Works Building, and continuing the survey of the field of equipment manufacturers.

At about mid-point in this period it was decided to defer the actual design of the proposed pilot plant. Emphasis was shifted from design to the compilation of engineering data obtained from bench-scale equipment. Thereafter, work was concerned with the transition from design to laboratory scale and the processing of simulated K-65 residue.

DETAILED REPORT

An equipment flow sheet representing the best information obtained from equipment manufacturers and the chemical research work was completed. This flow sheet covered only the residue treatment portion of the process. The information contained in this flow sheet is considered sufficient to enable draftsmen to perform a complete layout of the process up to the purification step. The chemical research work has indicated the need for a series of operations between the residue treatment and radium-barium

[REDACTED]

separation steps whose purpose is the removal of contaminants, chiefly lead, in the filtrate from the residue treatment process. That series of operations is referred to as the purification step. Preliminary expression in terms of engineering equipment of the data available on the purification step has exposed no undue difficulties.

A new equipment cost estimate was prepared for Area 1-C in the proposed Semi-Works Building. That estimate is not materially different in total amount although some changes were made in individual items from more complete data. In addition, an attempt was made to estimate installation, overhead, and operating costs. The estimates are preliminary and necessarily subject to inaccuracies because the flow sheet for the entire process has not been completed.

The writing of specifications for tanks and mixers was initiated.

Correspondence and interviews with equipment manufacturers were continued with beneficial results. In general, the abrasiveness and temperature of the materials in flow present the greatest engineering difficulties insofar as the selection of equipment is concerned. An analysis of the filtration characteristics of K-65 residue is desirable in order to obtain more precise recommendations from filter manufacturers.

Much of the work done in the transition from design to laboratory scale engineering research was concerned with the assembly of equipment that would process kilogram batches of residue. The pieces of equipment finally assembled were a 12-liter 3-necked flask heated by a Glascol mantel, a 0.5 square foot vacuum filter, a motor-driven mixer utilizing

a two-inch stainless steel propeller, and a four-liter vacuum receiver. Of these, only the filter will furnish an opportunity for securing quantitative engineering data.

A kilogram batch of simulated K-65 residue was prepared and carried through the process to the purification step. The results did not agree well with those obtained on actual K-65 residue.¹ Only 49 per cent of the lead was removed by the initial sodium hydroxide leach, and only 86 per cent was removed by the entire process (sodium hydroxide leach followed by two carbonations and two nitric acid leaches alternately). Sixty-nine per cent of the barium was removed by the first carbonation, and 93 per cent was removed by the entire process.

Although the primary purpose of the simulated runs was to test equipment and techniques, the results served to indicate the following:

1. Heating and/or mixing will have to be provided for filtrate receiver tanks because of the formation of precipitates.
2. A temperature of considerably above 100°F. is required at the nitric acid leach to drive off carbon dioxide. The nitric acid will eliminate the proposed use of rubber lined pumps at that point.
3. Deionizing equipment will be necessary for treating process water.

It should be pointed out that very little weight can be given quantitative results from processing simulated residue because of the great physical difference between the simulated and actual K-65 residues.

REFERENCE

1. Economides, M. and Martin, A. W.; Joy, E. F., Quarterly Report for General Research, MLM-475, pp. 15-25, 27-45.

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