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SUMMATION REPORT RECOVERY OF RADIUM FROM K-65 RESIDUE

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VITRO CORPORATION
OF AMERICA
NEW YORK CITY

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SUMMATION REPORT

RECOVERY OF RADIUM FROM K-65 RESIDUE

(23-E)

JOB 23

CONTRACT: AT(30-1)-848

PERIOD: March, 1950 through September, 1950

DATE: February 12, 1952

APPROVED: W. A. Bain
Project Manager

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ABSTRACT

Methods for recovering radium from K-65 residue have been investigated. A process using Versene was developed and demonstrated on a laboratory scale. In this process K-65 residue is leached with Versene solution and radium is adsorbed from the leach liquors and purified by the use of cation exchange resin.

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SUMMATION REPORT

RARE METAL RECOVERY - RESEARCH PROJECT 23E

JOB 23

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SUMMARY

This report summarizes work done by Vitro Corporation of America* on Research Project 23E, Rare Metal Recovery. This work, done under Atomic Energy Commission Contract AT(30-1)-848, is part of Vitro Job 23.

Research Project 23E had for its initial objective the scoping of approaches to radium recovery other than the classical Curie procedure and its modifications. This scoping program was carried out during the period March, 1950 through September, 1950 at which time work on the project was suspended.

In May, 1951 the project was reactivated with the objective of developing a complete laboratory process for radium recovery using Versene. This process was based on the results of the scoping program. This objective was substantially reached at the time laboratory operations were terminated in November, 1951.

* Effective August 31, 1951, the Kellex Corporation became Vitro Corporation of America.

SCOPING PROGRAM

Primary Separation

The methods investigated for the separation of radium from K-65 residue were as follows:

1. Leaching with H_2SO_4 at 90% or higher concentration, and diluting leach liquor to 70% acid to re-precipitate barium and radium sulfate.

2. Leaching with hot Versene solution to solubilize radium, barium, and lead.

3. Heating with ammonium chloride in the presence of a catalyst to a final temperature of 900°C, and leaching with water.

4. Fusion with sodium polyphosphates followed by leaching with water.

5. Heating with 85% phosphoric acid to 700°C and dissolving the glassy melt in water.

Of these methods of bulk separation, the H_2SO_4 leach and the Versene leach were most promising from a chemical and economic viewpoint.

Purification

The methods investigated for converting to a soluble form the barium and radium sulfates separated from K-65 residue by H_2SO_4, were as follows:

1. Fusion with excess calcium chloride at 650°C.

2. Heating with ammonium chloride in the presence of a catalyst to a final temperature of 900°C.

3. Fusion with sodium polyphosphates.

4. Heating with 85% phosphoric acid to approximately 700°C.

5. Boiling with excess 0.15 M Versene solution.

6. Treatment with excess anhydrous liquid HF at 19°C.

7. Treatment with anhydrous gaseous HF at 180-450°C.

The Versene treatment was the most promising for solubilizing bulk-separated barium and radium sulfates. Furthermore, it was found that cationic exchange resins were effective for the adsorption of radium from aqueous Versene solutions, and that the radium could be enriched by selective elution. However, since Versene solutions could be obtained from K-65 directly, there appeared to be no advantage in first separating barium and radium sulfates as such. Accordingly, the process selected for development was based on the use of Versene for leaching K-65 residue, and ion exchange resins for recovery and purification of the radium.

PROCESS DEVELOPMENT

Versene Leach

After a systematic study of the factors influencing the solubilization of radium in K-65 residue, the following conditions were determined to be optimum:

Slurry density	150 g of K-65 to 1 liter aqueous Versene
Versene concentration	0.15 M
Leach temperature	boiling
Leach time	1/2 hour
pH	8.0

Two stage leaching of K-65 residue under these conditions gave 85% solubilization of the radium with little or no silica going into solution. The use of higher Versene concentration and higher pH gave better radium recovery, but, also dissolved silica which interfered with subsequent treatment of the leach liquors.

Radium Concentration and Purification

A study of the reactions of radium and barium in Versene solution with cation exchange resins indicated that the conditions necessary for adsorption, stripping, and selective elution could be obtained by proper adjustment of pH.

Starting with Versene leach liquor in which the barium/radium ratio was about 80,000, a single stage of adsorption to saturation at pH 5.8 and stripping at pH 10 gave a product in which the barium/radium ratio was about 5,000 to 8,000. Readsorption to partly load another resin bed followed by selective elution at pH 5.8 or 6.2 gave a product in which the barium/radium ratio was less than 2.

The volumes of resin and elutant required appeared to be well within the range of commercial application. Accordingly, these steps were included in the laboratory scale process developed for radium recovery from K-65 residue.

Versene Recovery

For economical operation of the process it is necessary to recover and reuse the Versene used in leaching. In tests carried out to determine the efficiency of Versene recovery by precipitation of the free acid at pH 1.2, it was observed that when lead is present, Versene precipitation is incomplete and the precipitated Versene is impure. Hence, lead must be removed before precipitation of the Versene.

It was found that the addition of sodium sulfide to an alkaline Versene solution containing lead, precipitates lead sulfide and permits recovery of a higher purity Versene with better efficiency. However, optimum conditions of pH, temperature and time of digestion for lead removal had not been established at the time of project termination.

Best results obtained with recovered Versene have fallen short of those obtained with new material under comparable conditions, (55% radium solubilization as compared to 65% in a single stage leach). However, there is little doubt that if optimum conditions for Versene recovery were established, proper adjustment of Versene concentration would give satisfactory leaching.

LABORATORY OPERATIONS

For this study K-65 residue from the MCW refinery was used as the raw material. The sample used was in the form of a wet cake containing, as major constituents, silica, barium and lead sulfates and carbonates, and about 1/3 ppm of radium. An analysis of a 55 gal drum sample was made in the Vitro Laboratory and is given in Appendix A.

The analytical method used for radium determination was the method of Ames, et al, (1)* as modified in the Vitro Laboratory by Wamser, Keeler, Bernsohn, and Onacki. This method is presented in Appendix B.

SCOPING PROGRAM

The original objective of the present study was the scoping of new approaches to radium recovery. A further objective was the selection of one or two of the more promising methods (2) for detailed study and process development.

Primary Separation

Sulphuric Acid Leach (3a) (3f)

Bulk separation of barium-radium sulfates from K-65 residue was effected by leaching with H_2SO_4 (>90%), separation of the insolubles (silica, lead sulfate), and dilution of the extract to 70% H_2SO_4 concentration. The re-precipitated $BaSO_4$-$RaSO_4$ was filtered and the filtrate reserved for recon-

*This number and others appearing in similar manner in this report refer to the bibliography included in the Appendix of this report.

centration (by evaporation), and recycle. The data obtained indicated that by this treatment better than 95% of the radium in K-65 residue could be recovered as co-precipitated barium-radium sulfate.

This method appeared to have definite promise as a means of bulk separation of radium and barium from K-65 residue.

Versene Leach (3c) (3g)

Solubilization of radium in K-65 was effected by leaching with hot 0.15 M Versene previously adjusted to pH 7-8 to minimize uptake of silica. The slurry density was equivalent to 65 g K-65 residue per liter of Versene solution, and digestion time was about 20 minutes. The radium solubilized in a single leach amounts to about 65% of that present in the original K-65 residue. (Early results obtained before the improved analytical procedure for radium determination was established gave high values for the amount solubilized.)

Ammonium Chloride Treatment

K-65 residue mixed with about 10 times its weight of ammonium chloride was heated to a final temperature of 900°C in the presence of a platinum catalyst (4). About 50-60% of the radium was solubilized in a water leach of the treated residue. However, due to the high cost of the chemicals required and the difficulty of obtaining high radium recovery, this method did not merit further consideration.

Polyphosphate Fusion (3b)

Fusion of K-65 residue with sodium polyphosphates, e.g., $Na_5P_3O_{10}$ or $Na_6P_6O_{18}$, followed by leaching with water, solubilized most of the radium and barium as complex anions of the type $(BaP_3O_{10})^{\equiv}$ or $(Ba_2P_6O_{18})^{\equiv}$. The leach liquor, however, contained a difficultly filterable suspension of silica.

Phosphoric Acid Fusion (3b)

Heating K-65 residue with 85% phosphoric acid to $\sim 700^{\circ}C$ yielded a melt which could be leached with boiling 1N HCl and readily filtered to give a solution containing barium and radium in cationic forms and saturated with lead chloride. However, considerable technical difficulty was anticipated in carrying out the fusion on a commercial scale due to corrosion.

Purification

The most promising results from a chemical and economic viewpoint, in the primary separation of radium from K-65 residue, were obtained using a H_2SO_4 leach and a Versene leach, respectively. In the former case, the final product was in the form of solid radium-barium sulfate which had to be solubilized for subsequent treatment. In the latter case, the radium, barium and lead from K-65 residue were in solution in the form of complexes with Versene.

Recovery of Radium from Bulk Separated Ra-Ba Sulfates

The results of experiments to find suitable methods for solubilizing radium-barium sulfate are presented below. Preliminary findings in the treatment of the resultant solution by ion exchange are also presented.

Calcium Chloride Treatment (3c)

The barium-radium sulfates were heated with an excess of calcium chloride and held at $650^{\circ}C$ for 7 hours (5).

$$\left.\begin{matrix}Ba\\Ra\end{matrix}\right\} SO_4 + CaCl_2 \longrightarrow \left.\begin{matrix}Ba\\Ra\end{matrix}\right\} Cl_2 + CaSO_4$$

The reaction product was ground and leached with 80% methanol - 20% water. About 85% of the radium and 75% of the barium were present in the filtered liquor as chlorides.

Ammonium Chloride Treatment (3b) (3c)

The barium-radium sulfates were heated to 900°C with 10 times their weight of ammonium chloride in the presence of platinum or palladium catalyst (4). About 90% of the barium and radium in the bulk-separated sulfates was converted to water-soluble chlorides.

It was shown that the radium (and barium) from these chloride solutions could be quantitatively adsorbed on a cation exchange resin such as Dowex-50-Na. Some radium could be also be adsorbed on Dowex-50-Ba.

Polyphosphate Fusion (3b) (3d) (3e)

Fusion of the barium-radium sulfates with sodium polyphosphates (e.g. $Na_5P_3O_{10}$ or $Na_6P_6O_{18}$), followed by leaching with water, solubilized all the barium and radium as complex anions of the type $(BaP_3O_{10})^{=}$ or $(Ba_2P_6O_{18})^{=}$. The solution also contained $(SO_4)^{=}$.

Barium and radium were not readily adsorbed from these solutions by anionic resins since $(SO_4)^{=}$ was adsorbed along with the barium and radium. Passage of such a solution over IRA-400 in barium polyphosphate form resulted in immediate breakthrough of radium.

Phosphoric Acid Fusion (3b) (3d)

The barium-radium sulfates were heated with 85% phosphoric acid to approximately 700°C. Under these conditions the orthophosphoric acid was transformed into condensed polyphosphoric acids, e.g. $H_5P_3O_{10}$ and HPO_3. The resultant glassy melt was completely water-soluble. The solutions contained no $(SO_4)^{=}$ and on hydrolysis with HCl the barium and radium were converted to the cationic form and could be adsorbed on Dowex-50-H.

Versene Leach (3b)(3c)(3d)(3g)

The barium-radium sulfates were heated to boiling with an excess of 0.15 M Versene solution. Complete solubilization of the barium and radium was effected, the solution containing the anionic complexes of the metals, e.g. $(BaVe)^{=}$ (6) (7) (8) (9) (10).

These solutions contained $(SO_4)^{=}$ but careful adjustment of the pH to the lowest value which did not cause precipitation of barium and radium sulfates (of the order of 6.2) permitted the adsorption of barium and radium on cationic resins such as Dowex-50-Na. Dowex-50-Ba also adsorbed radium from these solutions.

Liquid HF Treatment (3c) (3f) (3g)

The barium-radium sulfates dissolved completely in 7.5 parts by weight of anhydrous HF at its boiling point (19°C). Volatilization of 80% of the HF from this solution resulted in the precipitation of the acid fluorides of barium and radium. The washed crystals were found to be completely soluble in hot, dilute HCl containing boric acid. The resultant solution contained 83% of the barium and 97% of the radium present in the original sulfates.

These solutions contained barium and radium as the fluoborates and their behavior with cationic resins was similar to that of the solutions containing the chlorides.

Gaseous HF Treatment (3f)

The barium-radium sulfates were contacted with anhydrous hydrogen fluoride at temperatures in the range 180-450°C. The reaction products in all cases were found to be mixtures

of barium and radium fluorides, fluosulfonates and sulfates, the relative proportions of which were dependent on the temperature and conditions of contacting.

The fraction of the sulfates converted to the fluorides and fluosulfonates could be solubilized by HCl-boric acid and water, respectively. The maximum radium that could thus be solubilized was about 65%. The presence of lead in the bulk-separated sulfates was found to interfere with the conversion of radium to a soluble form by this method.

The solutions of the water-soluble fluosulfonates hydrolyze too readily (with resultant precipitation of the sulfates and fluorides) to permit application of ion exchange technique. The solutions of the fluorides in HCl-boric acid behaved like solutions of the chlorides.

Recovery of Radium from Versene Leaches of K-65 Residue (3d)

Tompkins' report (11) on the separation of radium from barium by ion exchange presents interesting possibilities for use of this technique as a substitute for fractional crystallization in the commercial production of radium. Accordingly, the application of ion exchange technique to the recovery of radium from the Versene leach liquor was investigated.

Reduction of the pH of the Versene leach to the vicinity of 6.2 can be effected without precipitation of barium or radium as sulfates. Under these conditions the radium and some barium but not much of the lead, iron, etc., is adsorbed on a cation exchange resin (e.g. Dowex-50-Na).

Reduction of the pH of the column effluent to 4.0 precipitated $BaSO_4$. After filtration, further reduction to pH 1.2 precipitated Versene as the free acid. The fate of the lead was not determined.

[redacted]

Proposed Process

The result of the scoping program indicated that an attractive process for radium recovery from K-65 residue might possibly be developed. The most promising procedure for further investigation seemed to be:

1. Direct leaching of K-65 residue with hot 0.15 M Versene solution at pH 8.

2. Separation of radium from barium and purification by ion exchange.

3. Versene acid recovery at about pH 1.2.

A less desirable alternative might consist of the bulk separation of radium and barium sulfates, using H_2SO_4, and subsequent treatment of the resulting sulfates with Versene.

At about the time the above conclusions were reached (September, 1950) work on the project was suspended.

PROCESS DEVELOPMENT

In May, 1951 Project 23E was reactivated at the Vitro Jersey City Laboratory. The objective of the second phase of the project was to develop a complete laboratory process for radium recovery from K-65 residue using Versene for leaching, and ion exchange for separation and purification of the radium.

Detailed results of the investigation are presented in Vitro progress reports. (12) (13).

[redacted]

Versene Leach of K-65 Residue

Procedure

In the determination of the optimum conditions of pH, time of digestion, slurry density, Versene concentration and sodium to Versene ratio for solubilization of radium, K-65 residue was brought in contact with the Versene solution under predetermined conditions, after which the slurry was filtered rapidly under vacuum. The filtrate and the washed residue were analyzed for radium. The same general procedure, with appropriate modifications, was used in investigating the effect of K-65 residue pre-treatment, successive leaches, and fixed bed leaching.

Variation of Versene Concentration and Slurry Density

Wet K-65 residue in portions of 10, 15 or 30 g were brought in contact for 1 hour, at about 100°C, with 100 ml of Versene solution at concentrations varying from 0.05 M to 0.75 M. The slurry was filtered, the residue washed with three 50 ml portions of water, and the filtrate and residue analyzed for radium.

At the 300 g/liter slurry density, maximum solubilization of the radium, 71%, occurred at a Versene concentration of 0.75 M. At slurry densities of 100 g/l and 150 g/l, solubilization of 79% and 84%, of the radium respectively, occurred at 0.50 M Versene concentration. These data are shown in Fig. 1 and Table I.

Effect of Sodium to Versene Ratio

To determine the effect on radium solubilization of varying the sodium to Versene ratio, leaches were carried out at constant slurry density, Versene concentration, temperature and time of digestion, while the sodium to Versene ratio was varied from 2 to 5 mols of sodium per mol of Versene by the addition of NaOH to Versene acid. The results are given in Table II. Maximum solubilization of the radium, occurred at a sodium to Versene ratio of 4.

Variation of Digestion Time

The results of a series of tests to determine the optimum time of digestion for leaching K-65 residue with Versene are given in Table III. Maximum solubilization of the radium occurred with 1/2 hour digestion, decreasing gradually at longer periods. Evidently, time of digestion is not critical in the range of 0.5 to 6 hours. However, since the weight of residue increases with prolonged digestion, there must be re-precipitation of some material which carries radium.

Effect of pH on Radium Solubilization

Using a 150 g/liter slurry density and a solution of the tetrasodium salt of Versene, the effect of pH on the solubilization of radium from K-65 residue by Versene was investigated by adding HCl to a series of leaches to adjust the initial pH in the range of 7.0 to 12.8. The results are given in Table IV. It appears that the final pH should be in the range of 9 to 12 to give maximum solubilization of radium. However, to avoid simultaneous solubilization of silica the final pH should not exceed 8.5. Under these conditions radium solubilization is decreased somewhat, but the overall results are better.

Pre-Treatment of K-65 Residue

In an attempt to improve the solubilization of radium, K-65 residue was pre-treated with NaOH and Na_2CO_3. The results are given in Table V. Pre-treatment with NaOH was detrimental; pre-treatment with Na_2CO_3 gave some improvement, but probably not enough to warrant the expenditure for the chemical used.

Successive Leaches with Versene

Since it is important from an economic viewpoint to obtain maximum solubilization of radium, and since at best 80% can be solubilized in a single stage, successive leaching was investigated.

Radium solubilization over the range 85-95% was obtained, using 0.5 M Versene solution in 2 and 3 successive leaches, at various pH's and using various periods of digestion for the 2nd and 3rd leaches. However, considerable silica was solubilized under conditions giving 90 to 95% leaching efficiency. This silica precipitates upon pH reduction, carrying considerable radium.

With 0.15 M Versene solution, at pH 8, two-stage leaching gives about 85% solubilization and little or no silica is dissolved.

Fixed Bed Leaching

Table VI presents the results of a series of preliminary tests in which K-65 residue in a fixed bed on a steam-jacketed vacuum filter, was leached with hot 0.15 M Versene at pH 8. Solubilization proceeded at a rather slow rate. No doubt fairly complete solubilization could be obtained by fixed bed leaching, but the further development of this method would require study beyond the scope of the present investigation.

Discussion

From the results obtained, it would appear that maximum solubilization of radium from K-65 residue approximately 90%, may be achieved using 0.5 M Versene solution at about 100°C in successive leaches at a slurry density of 150 g/liter. Under these conditions, however, it was found that considerable SiO_2 was dissolved. This interfered seriously, since pH adjustment of the liquor resulted in precipitation of silica, which carried radium. Pre-treatment of the K-65 residue with NaOH, though it removed most of the silica, decreased the subsequent solubilization efficiency, while pre-treatment with Na_2CO_3, though it did not interfere with subsequent solubilization, was inefficient in removing SiO_2. Under the scoping program it had been shown that treatment for 1/2 hour with boiling 0.15 M Versene at pH8 did not dissolve appreciable SiO_2 from the K-65 residue. Subsequent tests with successive leaches, using boiling 0.15 M Versene at a slurry density of 150 g/liter, effected about 85% radium solubilization, with little or no SiO_2 in solution. Consequently, these conditions were selected for bulk separation of radium and barium from K-65 residue in the laboratory process under development.

Ion Exchange Purification

Feed Preparation

To prepare a feed for column runs, a large scale leach was carried out using 0.15 M Versene at pH 8. The leach liquor contained 10.2 μg of radium and 0.77 g of barium per liter, representing a barium to radium ratio of about 77,000. Other elements in the leach liquor were lead, 4.53 g/liter, and SiO_2, 0.088 g/liter. Runs also were carried out using various synthetic feed solutions. In preliminary experiments with Dowex-50 and IR-120, it was found that these resins gave comparable performance. In general, 1 x 100 cm resin columns were employed for the column runs.

Radium Concentration

To determine the extent to which radium might be concentrated in the leach liquors, a series of laboratory column runs were made with the liquor adjusted to pH 6.2 and 5.8, with concentrated HCl. The flow rate was approximately 0.75 gal/cu ft/min. At pH 6.2, after the passage of 5-bed volumes, there was radium breakthrough to the extent of 5% of the feed concentration. At pH 5.8, 20-bed volumes were passed before 7% breakthrough was detected. The column operated at pH 5.8 was completely stripped with 5-bed volumes of 6M HNO_3, and a barium to radium ratio of 18,000 was obtained in this strip liquor. This represents an enrichment factor of approximately 4.

In a similar column run at pH 5.8 which was run to 50% breakthrough and then stripped with 6 M HNO_3, the strip liquor had a barium to radium of 9,700. This represents an enrichment factor of approximately 8. A comparison of the results obtained at pH 5.8 is presented in the following table:

Throughput (Bed Volumes)	Breakthrough (%)	Resin Loading (μg Ra/ml)
20	7	0.2
50	50	0.44

Feed Volume/ Strip Volume	Strip Ba to Ra Ratios	Enrichment Factor
4	18,000	4
10	9,700	8

In a similar column run which was carried to 50% breakthrough and stripped with 5-bed volumes of 0.15 M Versene at pH 10, the barium to radium ratio in the strip liquor was 9,400. When this strip liquor was readjusted to pH 5.8 and passed over a 20-fold smaller column to 50% breakthrough, the strip liquor, 0.15 M Versene at pH 10, had a barium to radium ratio of 1,700. This represents an enrichment factor of 6 in the second cycle, or an overall enrichment of 48 in two cycles of adsorption and stripping without any selective elution. The volume reduction in the two cycles was about 100-fold.

Selective Elution

Ammonium Citrate and HCl as Selective Elutants

A series of laboratory column runs was carried out to determine the best conditions for selective elution when ammonium citrate and HCl were used as elutants. In each run, a synthetic feed solution containing 0.5 g of barium per liter (as $BaCl_2$) and Ba^{140} tracer was adsorbed on the top of a 1 x 100 cm column of IR-120. The selective elutant was then passed over the column to the point of barium breakthrough. An attempt was made to follow the progress of active material on the column with a survey meter, but the presence of the daughter La^{140}, and the activity spread on the column obscured the results.

Runs were made with 4M HCl at flow rates of 0.4 and 0.05 gal/cu ft/min. In both cases the barium appeared in the eluate at the 5th-bed volume.

Runs with 0.5M ammonium citrate solution at pH 5 also were made at flow rates of 0.4 and 0.05 gal/cu ft/min. At the faster rate, barium appeared in the 3rd-bed volume; at the slower rate, barium appeared in the 5th-bed volume. In another run with the ammonium citrate solution at pH 3.5 and the slow rate, barium appeared at the 9th-bed volume.

In further studies of radium-barium separation by selective elution, the above (synthetic feed) runs were duplicated, using as feed, process solutions of HNO_3 strip liquors from previous adsorption runs. These feed liquors were obtained in some cases by evaporating the HNO_3 strip liquor to 30-50 ml and then diluting to 1 liter; in other cases the HNO_3 strip liquor was evaporated to 12 M, cooled, and the $Ba(NO_3)_2$ crystals formed were separated and dissolved in 1 liter of water. In all cases, the resulted solution had a pH of 0.5 - 1.0, and re-adsorption occurred in the upper six inches of the resin column. In general, the results duplicated those obtained with the synthetic feed solution, but very little separation of radium from barium was found. Enrichment factors were of the order of 2.5 to 3.5.

Versene as Selective Elutant

To determine the effectiveness of Versene as a selective elutant, a series of laboratory column runs was made in which the feed consisted of 0.15 M Versene solution, at pH 5.8, containing 177 mg barium (as $BaCl_2$) and radium tracer. Four-bed volumes of this feed were passed over each of these columns at a rate of approximately 0.1 gal/cu ft/min. The columns were then eluted with:

(a) 0.15 M Versene, pH 5.8, at 0.94 gal/cu ft/min

(b) 0.15 M Versene, pH 6.2, at 0.28 gal/cu ft/min

(c) 0.15 M Versene, pH 6.2, at 0.1 gal/cu ft/min

In (a), barium appeared in the 1st-bed volume, rose to a peak concentration in the 8th-bed volume, and could not be detected in the 18th-bed volume. The radium tracer appeared to leak through the column at a fairly constant low rate up to the 16th-bed volume, in which a significant increase occurred. (This was also the last portion in which barium appeared, as determined by a qualitative test sensitive to 2 ppm.)

In (b), barium appeared in the 1st-bed volume, rose to a peak concentration in the 3rd-bed volume, and could not be detected in the 8th-bed volume. The first significant appearance of radium tracer occurred in the 7th-bed volume, which was also the last bed volume in which the barium could be detected.

In (c), barium appeared in the 1st-bed volume, rose to a peak concentration in the 3rd-bed volume, and could not be detected in the 7th-bed volume. The first significant appearance of radium tracer occurred also in the 7th-bed volume.

The results of these column runs indicated that barium and radium separation could be effected by selective elution with Versene solution. Since, in (c) there was apparently complete separation of barium and radium, a column run was carried out under the conditions used therein, but with a process solution strip liquor as feed (barium to radium ratio approximately 7,000). A similar run was carried out using 0.15 M Versene solution at a pH of 5.8 as elutant. In each case the final product was stripped from the column with 6M HNO_3.

Determination of Product Purity

To determine the purity of the final product, the HNO_3 strip liquor was evaporated to dryness in a platinum crucible, the residue treated with concentrated H_2SO_4, which was then diluted to 2M, and the turbidity of the resultant solution compared to a standard sample prepared under the same conditions. The product from both column runs showed no turbidity under conditions which gave a positive test with 40 μg of barium. Upon filtering the H_2SO_4

solution and igniting and weighing the filter paper in the same platinum crucible used in the original treatment, no increase in weight could be detected on an ordinary analytical balance sensitive to 0.1 mg. The final product in both cases contained less than 40 μg of barium; it contained 16 μg of radium in the case of the elution carried out at pH6.2 and 20 μg with the elution at pH 5.8. Consequently it may be concluded that the barium to radium ratio was less than 2.5 in the former run and less than 2.0 in the latter run. The elution curve for the run at pH 5.8 is presented in Fig. 2.

Preliminary experiments were performed with Ba^{140} tracer to develop a method for determining barium in unweighable amounts of high purity radium produced from radium-barium mixtures containing barium tracer. The procedure followed was similar to that used in the radium determination presented in Appendix B. The activity was precipitated with $BaCl_2$ carrier from an HCl-ether solution. It was found that:

1. Ba^{140} was separated almost completely from La^{140} daughter. Aluminum absorption measurements indicated about 97-98% La^{140} removal.

2. Up to 30,000 c/m of beta-gamma activity of the Ba^{140} did not interfere with alpha counting.

3. Standard radium samples up to 5,000 alpha c/m processed by the above procedure gave about 5 beta-gamma counts per 100 alpha counts. This indicates the extent to which radium interferes with Ba^{140} counting.

Although the method was not proved, it seems likely that such a method could be developed.

Discussion

From the date above it appears that ion exchange may be used for recovery and purification of radium from Versene leach liquors.

The process envisioned includes three cycles of exchange in which the columns are operated to saturation at pH 5.8 and stripped at pH 10. These steps should bring about reduction of solution volume to the point where the radium and barium can be adsorbed in the upper portion of a column. Following this, selective elution of barium, using 0.15 M Versene at pH 6.2 as elutant, should leave high purity radium on the column, from which it can be recovered by stripping.

Versene Recovery

Since commercial grade Versene is a fairly expensive chemical (about $0.62 per pound), a commercially practicable process requires some cheap method of Versene recovery. According to the literature (14), (15), Versene acid is soluble only to the extent of 0.3 g/liter in water at room temperature, and is generally prepared by precipitation at pH 1.2. The experiments described below were performed to determine whether Versene might be recovered from process leach liquor by precipitation.

Versene Acid Precipitation

In preliminary experiments with actual leach liquors, in which (1) the pH was adjusted to 5.8 with HCl, (2) the pH was adjusted to 4.4 with H_2SO_4, (3) the precipitated $BaSO_4$ was filtered off, and (4) the pH was adjusted to 1.2 with H_2SO_4, the recovered Versene acid was generally 60-70% of the initial amount. Since technical grade Versene was used in these experiments, it was suspected that the low recoveries might be due to soluble impurities in the starting material. Accordingly, Versene acid was precipitated from water solutions in which technical grade Versene and recrystallized Versene were used as starting materials. The results of these tests were as follows:

Versene (grade)	Recovered (%)
Technical	67
Recrystallized once	95
Recrystallized twice	99

Since the above results indicate that the technical grade contains soluble acids, all subsequent experiments on Versene recovery were performed with analytical grade Versene.

Effect of Lead on Versene Acid Precipitation

One hundred ml portions of a water solution of analytical grade Versene containing 3.5 g of $PbNO_3$ and 4.38 g of Versene acid were adjusted to pH 8 with NaOH. HCl was added to one portion to give pH 1.2. HCl was added to a second portion and adjusted to give pH 4.4, then it was treated with H_2S, the PbS filtered off, and the filtrate adjusted to pH 1.2. Versene recovery and purity were determined to be as follows:

Treatment	Versene Recovery (%)	Versene Purity (%)
None	57	96.
H_2S	97	99.9

Apparently, the presence of lead in Versene solution inhibits the precipitation of Versene acid, and the Versene recovered is impure.

Removal of Lead from Leach Liquor

Acid Medium

Versene leaches were carried out at pH 8 with 0.15 M Versene in the usual manner and the filtrates were adjusted, first to pH 5.8 with concentrated HCl, and then to pH 4.4 with concentrated H_2SO_4, to simulate the sequence of steps involved when radium is adsorbed from leach liquors by ion exchange resins. In one case, the $BaSO_4$ was filtered off and the filtrate treated with H_2S; in another case, the slurry containing the $BaSO_4$ was treated directly with H_2S. In both cases the final precipitate was filtered off and the filtrate adjusted to pH 1.2 with concentrated H_2SO_4 to precipitate Versene acid. Recovery was about 100%, but

the product contained about 15% impurity. The former procedure was repeated and the recovered Versene reconstituted and recycled through two additional leach and recovery stages. The results were as follows:

Cycle	Versene	μg of Ra/g of Residue	Ra Solubilized (%)
1	Fresh	0.19	60
2	Recovered once	0.29	39
3	Recovered twice	0.59	--

Apparently, there is an impurity buildup in the recovered Versene which prevents the solubilization of radium. A qualitative spectrographic analysis of the ash from the Versene acid, recovered after the 3rd cycle, shows lead to be the principal impurity.

Alkaline Medium

A leach was carried out in which 5 g of Na_2S were added to 100 ml of 0.15 M Versene slurry containing K-65 residue. The final pH of the supernatant liquor was 9.9.

After filtration, the liquor was adjusted to pH 5.8 with concentrated HCl, then to pH 4.4 with concentrated H_2SO_4. Next the $BaSO_4$ was removed and the pH was adjusted to 1.2 with concentrated H_2SO_4. The resultant Versene acid was 99.8% pure. In the above experiment a digestion period of 1 to 2 days occurred after each precipitation.

In a similar operation, except that the pH of the slurry was maintained at about 8 during the leaching and the digestion period after each precipitation step was kept to about 1 hour, the Versene was recovered and reused in a second and third leaching cycle with the following results:

Cycle	Versene	µg of Ra/g of Residue	Ra Solubilized (%)
1	Fresh	0.32	30
2	Recovered once	0.28	31
3	Recovered twice	0.20	49

Apparently, either the decreased digestion times at various stages left greater amounts of impurities in the recovered Versene or the lower pH of the leach, in the presence of PbS, resulted in low solubilization of radium.

In another experiment, leaching was carried out in the absence of sulfide and H_2S was passed into the filtered leach liquor at ~ pH 8 with the following results:

Cycle	Versene	µg of Ra/g of Residue	Ra Solubilized (%)
1	Fresh	0.21	62
2	Recovered once	0.27	55
3	Recovered twice	0.50	7

Discussion

The results of the tests on Versene recovery are inconclusive. It appears that removal of lead as PbS under alkaline conditions should be effective in giving good recovery and high purity. However, the optimum conditions for recovery and subsequent re-use of Versene have not been established. Laboratory operations were terminated by the AEC before investigation of the factors involved in Versene recovery could be completed.

Proposed Radium Recovery Process

On the basis of the process development studies, a complete Versene process was established for the recovery of radium from K-65 residue. This process is outlined below. It should be emphasized that the

conditions selected are probably not optimum. However, they should form a satisfactory basis for the initiation of future pilot studies in a system designed to permit reasonable procedure modification.

Versene Leach

At a slurry density of 1.25 pounds wet residue per gallon of leach liquor, treat K-65 residue twice with boiling 0.15 M Versene solution at pH 8 for one-half hour each in two successive batch leaches. (Counter-current 2-stage leach is recommended but has not been tested.)

Ion Exchange — Radium Concentration

Adjust the filtered leach liquor to pH 5.8 and pass over resin IR-120 at a flow rate of 0.75 gal/cu ft/min. About 20-bed volumes should be passed to radium breakthrough.

Strip with 0.15 M Versene solution at pH 10 and a flow rate of 0.4 gal/cu ft/min. About 5-bed volumes of strip feed are required.

Repeat once or twice, readsorption of radium at pH 5.8 and stripping at pH 10 to reduce strip liquor volume so that the radium may be adsorbed in the upper portion of a relatively small diameter column, preparatory to selective elution.

Note: The conventional method of 3-column operation, in which two columns are operated in series for adsorption while the third is being regenerated, is recommended for concentration of radium from the leach liquor.

Radium Purification

Selective Elution

Adjust final strip liquor to pH 5.8 and pass over column of

IR-120 equal to about one-fourth the volume of the feed solution, at a flow rate of 0.1 gal/cu ft/min.

Pass fresh 0.15 M Versene solution at pH 6.2 over the partly loaded column, at a flow rate of 0.1 gal/cu ft/min, until radium appears in the effluent. (About 7-bed volumes of elutant are required.) The radium left on the resin should be high in purity.

Strip with 0.15 M Versene solution at pH 10 and a flow rate of 0.4 gal/cu ft/min. (About 5-bed volumes are required.)

Product Concentration

Adjust strip liquor to pH 5.8 or lower to put radium in cationic form, and pass over column of IR-120 at a flow rate of 0.75 gal/cu ft/min to radium breakthrough.

Strip column with 6-bed volumes of 6 M HNO_3 at a flow rate of 0.4 gal/cu ft/min.

Evaporate strip liquor to obtain product.

Versene Recovery

Treat column effluents with Na_2S, or perhaps Na_2S_x, in an amount sufficient to give an excess over that required to precipitate lead sulfide, and adjust to pH 8.

After digestion at 90°C, filter and adjust the filtrate to pH 4.5 with H_2SO_4 to precipitate $BaSO_4$.

After digestion at 90°C, filter and adjust the filtrate to pH 1.2 with H_2SO_4 to precipitate Versene acid.

After digestion at room temperature, filter the Versene Acid and return to the leach solution make-up.

Note: This procedure for the recovery of Versene has not been fully investigated. However, with minor modifications it should give satisfactory results.

Recommendations

Although it is felt that the process is ready for piloting, it would appear desirable to investigate a number of items more fully in the event that a pilot program is initiated.

Versene Leach

Demonstration of Batch Countercurrent Leach

Solubilization of 85% of the radium in K-65 residue was shown in two successive leaches. It remains to be demonstrated that these leaches can be satisfactorily carried out countercurrently.

Fixed Bed Leach Under Pressure

The results of the fixed bed leach tests appear sufficiently promising to warrant further research with a pressure system. Passage of the leach solution over the bed under pressure, rather than under vacuum, should result in better contact of leach solution with the solids. Temperatures higher than 100°C could then be used. Higher temperatures might very well give more efficient leaching.

Product Purification by Ion Exchange

A systematic investigation would be desirable to determine optimum pH, column length, and flow rate for selective elution. It should be possible to find conditions which would give a satisfactory product in a 24 hour cycle.

Product Purity

It would be desirable to complete the development of a Ba^{140} tracer method for use in determining product purity at a radium to barium ratio of 10-20 to 1 in operations on a laboratory scale.

Versene Recovery

A systematic investigation of the variables involved in lead removal from column effluents, before Versene acid precipitation, would be required to establish a satisfactory procedure for economical operation.

TABLE I

EFFECT OF VERSENE CONCENTRATION AND SLURRY DENSITY ON SOLUBILIZATION OF RADIUM FROM K-65 RESIDUE

μg of Ra/g of K-65 Residue: 0.32
Duration of Leach: 1 hour
Temperature of Leach: Boiling

Versene Concentration (M)	pH	Ra Concentration: Filtrate (g/ml)	Ra Concentration: Residue (μg/g)	Residual Solids (g/100 g of K-65 Residue)	Ra Solubilized (%)
Slurry Density of 100 g/liter of Added Solution					
0.05*	11.1	0.35×10^{-8}	0.54	56	6*
0.15	11.3	2.1×10^{-8}	0.19	48	72
0.30	11.7	2.5×10^{-8}	0.13	49	80
0.50	12.3	2.4×10^{-8}	0.14	38	84
0.75	12.9	2.5×10^{-8}	0.23	43	69*
Slurry Density of 150 g/liter of Added Solution					
0.05	11.0	0.43×10^{-8}	0.66	60	--*
0.15	11.1	0.74×10^{-8}	0.24	53	60
0.30	11.3	2.8×10^{-8}	0.20	53	67
0.50	11.7	3.5×10^{-8}	0.13	53	79
0.75	12.1	3.5×10^{-8}	0.13	53	79
Slurry Density of 300 g/liter of Added Solution					
0.05	11.0	0.02×10^{-8}	0.6	63	--*
0.15	11.2	1.1×10^{-8}	0.47	60	15
0.30	11.2	0.2×10^{-8}	0.29	56	49
0.50	11.5	--	0.19	53	69
0.75	11.6	5.1×10^{-8}	0.20	46	71

* These data are not included in Fig. 1.

TABLE II

EFFECT OF SODIUM TO VERSENE RATIO ON SOLUBILIZATION OF RADIUM FROM K-65 RESIDUE WITH VERSENE

μg of Ra/g of K-65 Residue:	0.32
Slurry Density:	150 g/liter of added solution
Versene Concentration:	0.50 M
Duration of Leach	1 hour
Temperature of Leach:	Boiling

Na (Mol/Mol Versene)	pH	Ra Concentration: Filtrate (g/ml)	Ra Concentration: Residue (μg/g)	Residual Solids (g/100 g of K-65 Residue)	Ra Solubilized (%)
2	5.9	0.38×10^{-8}	0.56	61	--
3	7.5	2.1×10^{-8}	0.29	42	63
4	10.5	3.4×10^{-8}	0.19	37	79
5	11.9	1.9×10^{-8}	0.48	51	23

TABLE III

EFFECT OF DIGESTION TIME ON SOLUBILIZATION OF RADIUM FROM K-65 RESIDUE WITH VERSENE

μg of Ra/g of K-65 Residue:	0.32
Slurry Density:	150 g/liter of added solution
Versene Concentration:	0.50 M
Temperature:	Boiling

Digestion Time (hr)	pH	Ra Concentration Filtrate (g/ml)	Ra Concentration Residue (μg/g)	Residual Solids (g/100 g of K-65 Residue)	Ra Solubilized (%)
0.5	11.0	3.6×10^{-8}	0.16	49	75
3	10.8	3.4×10^{-8}	0.16	59	71
6	10.9	3.3×10^{-8}	0.16	64	69

TABLE IV

EFFECT OF pH ON THE SOLUBILIZATION
OF RADIUM FROM K-65 RESIDUE WITH VERSENE

μg of Ra/g of K-65:	0.32
Slurry Density:	1.50 g/liter of added solution
Versene Concentration:	0.5 M
Temperature of Leach:	Boiling
Duration of Leach:	1 hour

pH		Ra Concentration		Residual Solids (g/100 g of (K65 Residue)	Ra Solubilized (%)
Initial	Final	Filtrate (g/ml)	Residue (μg/g)		
7.0	8.5	2.5×10^{-8}	0.25	62	52
8.1	9.1	3.2×10^{-8}	0.12	59	77
9.0	10.2	3.6×10^{-8}	0.11	58	80
10.2	10.9	3.7×10^{-8}	0.16	59	71
12.8	12.0	4.0×10^{-8}	0.15	49	77

TABLE V

EFFECT OF PRE-TREATMENT OF K-65 RESIDUE
UPON SOLUBILIZATION OF RADIUM WITH VERSENE

Slurry Density: 150 g/liter of added solution

Pre-Treatment	% Ra Solubilized	
	0.15 M Versene	0.50 M Versene
None	60	79
Boiling 20% NaOH for 3 hr	--	65
Boiling 20% Na_2CO_3 for 10 hr	78	82

TABLE VI

SOLUBILIZATION OF RADIUM

FROM A FIXED BED OF K-65 WITH VERSENE

Bed Diameter: 3.25"

Versene Concentration: 0.15 M

Temperature of Leach: 90° C

Leach Solution pH: 8

K-65 (g)	0.15 M Versene Passed (ml/g)	Ra Solubilized (%)
15	27	79
30	17	66
50	14	58

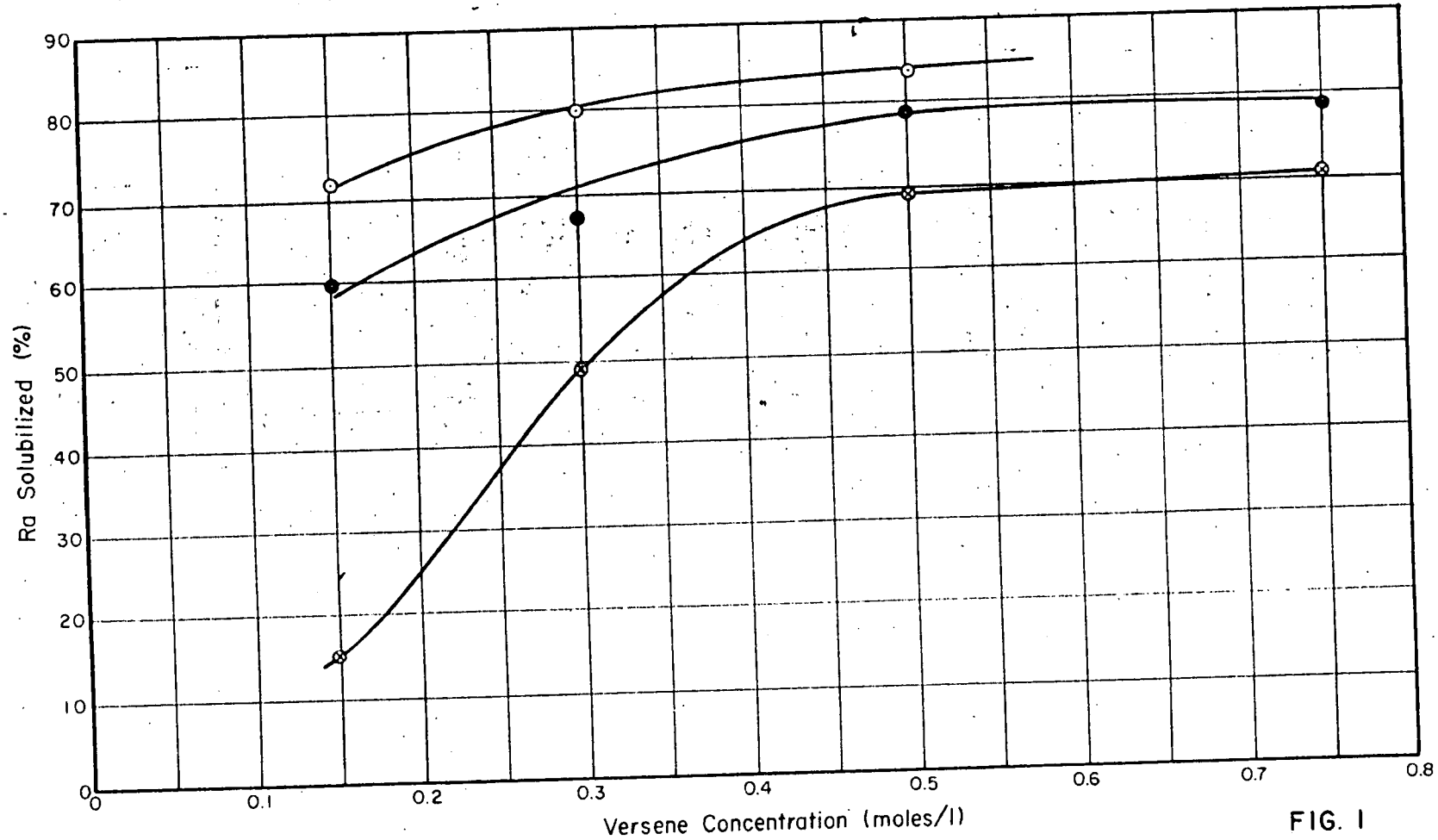

FIG. 1

Leach:
Duration - 1 hour
Temperature - Boiling
Slurry Density:
⊗ 300 g/l
● 150 g/l
⊙ 100 g/l

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Effect of Versene Concentration on Solubilization of Radium from K-65 Residue

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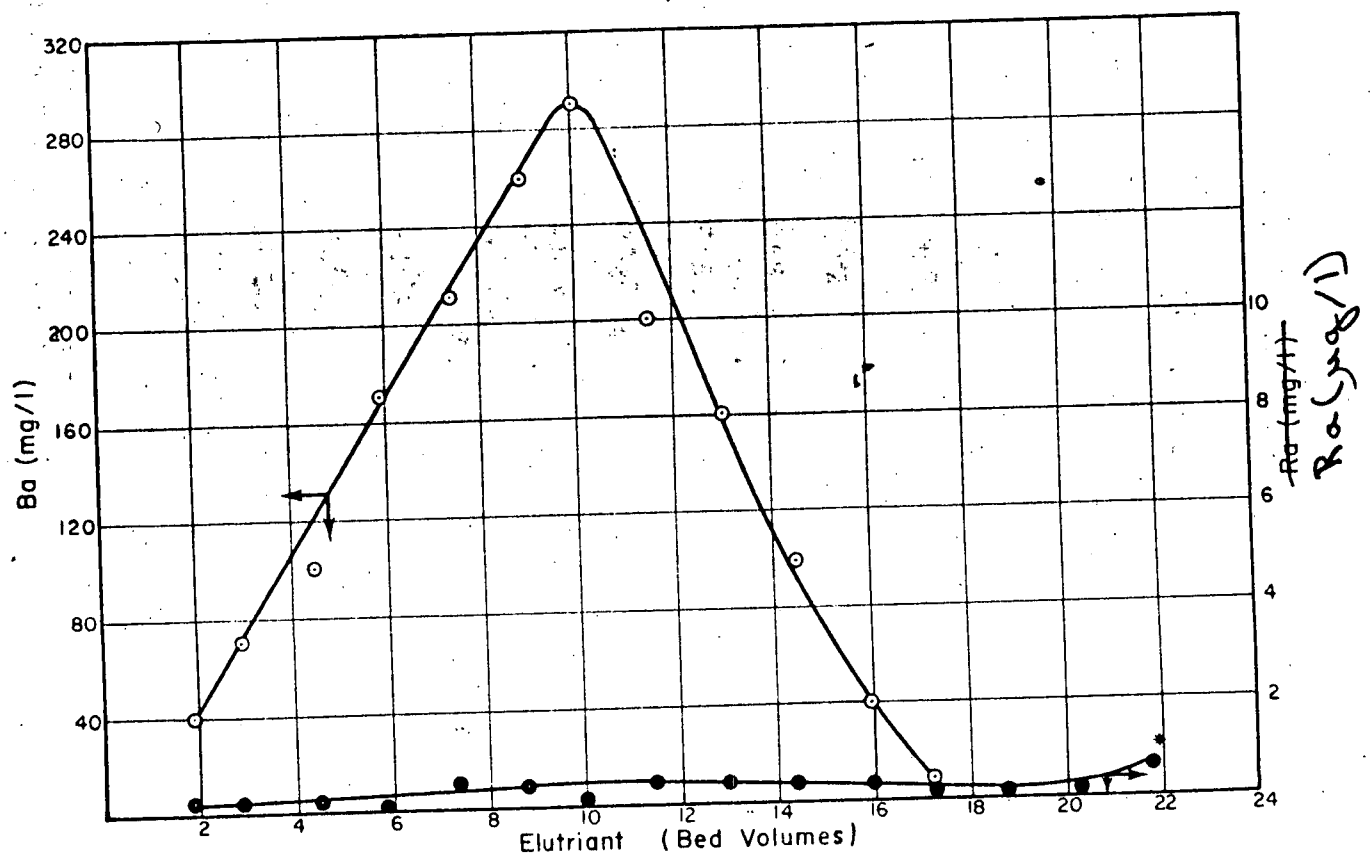

Column: IR-120 1 x 100 cm
Feed: 0.15 M Versene, pH 5.8, 262 ml
0.48gBa/liter
8.8×10^{-5} g Ra/liter
Elutriant: 0.15 M Versene, pH 5.8
Flow Rate: 0.1 gal/cu ft./min (1ml/ min)
* Strip Solution: 6 M HNO_3 (0.4 gal/cu. ft./min)
○ Ba Concentration
● Ra Concentration

FIG. 2

VITRO CORPORATION OF AMERICA		
Selective Elution of Barium and Radium with Versene		
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APPENDIX A

ANALYSIS OF K-65 RESIDUE

		%
Loss at	110°C	31.8
Further Loss at	400°C	3.4
	SiO_2	36.4
	$BaSO_4$	7.7
	$PbSO_4$	1.4
	Na_2SO_4	0.13
	$PbCO_3$	11.0
	Na_2CO_3	0.92
	U_3O_8	0.25
	R_2O_3	3.54
	MoO_3	1.13
	Ra	0.000030

Other metals positively identified Ca, Ni, Co, Mn, V

APPENDIX B

DETERMINATION OF RADIUM IN RESIDUES

Dissolution of the Sample in Condensed Phosphoric Acids

SUMMARY

A method was developed for the determination of radium in residues containing silica, barium and lead sulfates, and other oxides and sulfates. The sample is heated in a platinum vessel with orthophosphoric and hydrofluoric acids. On continued heating, silica, excess HF, and sulfate are evolved and the resultant clear viscous melt is completely soluble in water. Radium may be determined in an appropriate aliquot of this solution by the standard barium chloride carrier precipitation procedure.

PRIOR ART

The most accurate method for radium assay is the emanation technique, in which the radon generated by the radium is separated, collected and measured. However, a much more rapid method for radium, one which is suitable for much practical work, is based on the co-precipitation of radium on barium chloride carrier followed by alpha counting.*

Application of this rapid radiometric method requires the radium in solution, and common practice in the preparation of samples of gangues (which may contain silica, barium and lead sulfates and other oxides and sulfates) usually involves either:

* "Rapid Radiometric Assay for Radium and Application to Uranium Ore Process Solutions", Paper 22.70, p. 1700-16 in "The Transuranium Elements", Part II, IV-14B, McGraw-Hill Book Company, Inc., New York, 1949.

1. Preliminary leaching with hot ammonium acetate (to effect the removal of some of the lead sulfate), followed by HF-H_2SO_4 treatment for silica removal, fusion of the ignited residue with Na_2CO_3, extraction of the melt with water and the separation of the barium-radium-lead carbonates. The thoroughly washed carbonates are dissolved in dilute HCl and an aliquot portion of the solution is taken for analysis.

2. Ignition of the sample with an excess of zinc dust (effecting sulfate removal by volatilization), followed by leaching with dilute acid, treatment of the insolubles with HF and dissolution of the residue in acid.* An aliquot of the combined solutions is taken for analysis.

VITRO METHOD

The method devised was developed to facilitate the preparation of such gangue and residue samples for analysis by the rapid radiometric procedure, and has the advantage that, in one operation, silica, excess HF, and sulfate are volatilized and the resultant material is completely water-soluble.

Reagents

85% orthophosphoric acid, reagent grade
48% hydrofluoric acid, reagent grade
HCl - ether solution— 6 volumes of 12N HCl and 1 volume of diethyl ether
1.5 M barium chloride solution

Procedure

Up to 0.5 of the sample is accurately weighed and transferred to a 30 ml platinum crucible. Approximately 10 ml of 85% orthophosphoric acid and 3-5 ml of 48% hydrofluoric acid are added, and the crucible heated gradually

* "An Emanation Method for Radium Analysis", Paper 16.7, p. 1206-1225 in "The Transuranium Elements", Part II, IV-14B, McGraw-Hill Book Company, Inc., New York, 1949.

so that gentle boiling of the contents is maintained. When silica and most of the excess HF has been volatilized (volume of the residual charge about 7 ml), the mixture is gradually brought to a dull red heat and maintained at this temperature for 15-30 minutes, or until a clear viscous, fuming liquid is obtained. The cooled glassy melt is dissolved in about 50 ml of water and the solution diluted to some convenient volume (i.e., so that 1 ml will contain 10^{-10} to 10^{-8} grams of Ra).

A 1 ml aliquot of this solution is transferred to a 15 ml graduated centrifuge tube. About 0.05 ml of 1.5 M $BaCl_2$ is added (equivalent to about 10 mg Ba). In the event that the aliquot taken for analysis contains more than a few milligrams of barium, proportionately less 1.5 M $BaCl_2$ should be added. Seven ml of cold (0°) 6:1 HCl-ether is added, the mixture stirred, and the precipitated barium-radium chlorides (monohydrates) handled as described in "Rapid Radiometric Assay for Radium and Application to Uranium Ore Process Solutions."*

The alpha activity of the mixture may conveniently be determined in a parallel plate counter, or a methane-argon proportional counter, or the more newly developed scintillation counter.

Discussion

The glassy melts obtained from the treatment described above are soluble in water, and the resultant solutions presumably contain the Ra, Ba, Pb etc. in the form of anionic complexes, e.g., $(Ba_2P_6O_{18})^{=}$ or $(BaP_3O_{10})^{=}$.** Thus,

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* Paper 22.70, p. 1700-16 in "The Transuranium Elements", Part II, IV - 14B, McGraw-Hill Book Company, Inc., New York, 1949.

** D. Yost and H. Russell "Systematic Inorganic Chemistry", p. 221, Prentice Hall, Inc., 1944.

the Ba in such solutions is found to be masked against precipitation by sulfate. The polyphosphoric acid salts of these metals are undoubtedly formed by the progressive dehydration of the orthophosphoric acid which yields condensed phosphoric acids.*

$$H_3PO_4 \rightarrow H_4P_2O_7 \rightarrow H_5P_3O_{10} \longrightarrow (HPO_3)_6$$

Further, those condensed phosphoric acids which are formed at temperatures in the range of the boiling point of sulfuric acid probably initiate the displacement and eventual volatilization of the sulfate, e.g.:

$$2\ HPO_3 + BaSO_4 \longrightarrow Ba(PO_3)_2 + H_2SO_4\uparrow$$

Although the radium is present in the prepared solution largely as an anionic polyphosphate complex, it was not found necessary to decompose these complexes prior to the precipitation of the radium as its chloride (as for example by boiling the solution to rehydrate all the phosphates to the ortho form). Presumably, in the presence of a 6-fold excess of 12N HCl, all the radium is cationically available.

Results Obtained

The rapid radiometric assay of radium is described as being sensitive to 10^{-12} grams Ra (the specific alpha acitvity of Ra is 2.165×10^{-12} dis./min) and capable of 3-10% accuracy. The method further affords separation of radium from all other α-emitting substances accompanying it in nature, hence this phase of the determination involves no interferences.

The method herein described comprises a rapid preparation of certain samples for the radiometric assay and was found capable of quantitative solution of the radium in a variety of materials. Known amounts of radium (from standard solutions prepared by diluting the contents of Bureau of Standards radium ampoules) added to various samples and carried through the entire procedure were recovered to within 10%.

* R. Bell, Ind. Eng. Chem. 40, 1464 (1948).

Since the geometry and influence of self-absorbtion and back-scattering are dependent on the type of counting instrument and planchet used, the counting rates of samples were related to radium content by means of a factor determined under the same conditions for known amounts of radium.

Typical results obtained are summarized in the table on the following page.

Although hot polyphosphoric acids are highly corrosive, no difficulty with platinum ware was experienced. Over 200 $HF-H_3PO_4$ fusions were effected during the project without injury to any of the platinum ware. It is recommended, however, that residues containing both orgainc matter and lead sulfate, be pretreated with $HNO_3-H_2SO_4$ before the addition of HF and H_3PO_4.

The method appears to give consistent results.

RECOVERY OF ADDED RADIUM — $HF-H_3PO_4$ DISSOLUTION

FOLLOWED BY $BaCl_2 \cdot H_2O$ CARRIER PRECIPITATION

Sample	Radium Added* ($g \times 10^{-10}$)	α Counting Rate (counts/min)	Increased Activity Due to Added Radium (counts/min)
Residue 1	None	411	
Residue 1	5	733	322
Residue 2	None	322	
Residue 2	5	622	300
Residue 3	None	378	
Residue 3	5	675	297
Residue 4	None	563	
Residue 4	5	864	301
Residue 5	None	309	
Residue 5	5	613	304
Residue 6	None	150	
Residue 6	5	489	339
		Average	310 ± 13

* Standard radium samples of 5×10^{-10} grams processed by the same procedure in the absence of foreign material gave 302 counts/min.

APPENDIX C

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   3f. KLX-1206 - "Progress Report - August, 1950 - Job 23" dated Sept. 11, 1950.
   3g. KLX-1207 - "Progress Report - September, 1950 - Job 23" dated Oct. 9, 1950.

4. F. Feigl - "Specific, Selective and Sensitive Reactions", Academic Press, N. Y., 1949.

5. Ind. Eng. Chem. 35, 608-613 (1943).

6. Eister, W. K. (Technical Division, ORNL)" Progress Report for Month Ending September 30, 1949", ORNL 519.

7. Ibid., "Progress Report for Month Ending October 31, 1949", ORNL 523.

8. Ibid., "Progress Report for Month of December, 1949", ORNL 640.

9. Higgins, Blanco, Unger - "Preliminary Demonstration of RaLa Ion Exchange Processes at the Kilocurie Level" - ORNL 623, March 22, 1950.

10. Blanco - "Laboratory Development of an Ion Exchange RaLa Process" ORNL 620 - June 2, 1950.

11. Tompkins - "Separation of Radium from Barium by the Use of an Ion Exchange Column Procedure" - AECD 1998, October 31, 1947.

12. Vitro Monthly Progress Reports.

12a. KLX-1217 - "Progress Report - May, 1951 - Job 23" dated June 27, 1951.

12b. KLX-1219 - "Progress Report - June, 1951 - Job 23" dated July 23, 1951.

13. Letter sent weekly to D. C. Moore, Director, Engineering and Construction Division, New York Operations Office, Atomic Energy Commission, with enclosed Weekly Progress Reports:

KLX-724-N, dated June 15, 1951
KLX-739-N, dated June 25, 1951
KLX-745-N, dated June 30, 1951
KLX-749-N, dated July 7, 1951
KLX-754-N, dated July 14, 1951
KLX-761-N, dated July 23, 1951
KLX-771-N, dated July 28, 1951
KLX-776-N, dated August 3, 1951
KLX-788-N, dated August 11, 1951
KLX-801-N, dated August 18, 1951
KLX-807-N, dated August 24, 1951
KLX-821-N, dated August 31, 1951
KLX-23-3-N, dated September 10, 1951
KLX-23-5-N, dated September 17, 1951
KLX-23-10-N, dated September 24, 1951
KLX-23-15-N, dated October 1, 1951
KLX-23-17-N, dated October 6, 1951
KLX-23-20-N, dated October 15, 1951

KLX-23-22-N, dated October 19, 1951
KLX-23-27-N, dated October 25, 1951
KLX-23-32-N, dated November 3, 1951
KLX-23-35-N, dated November 10, 1951
KLX-23-48-N, dated November 17, 1951
KLX-23-39-N, dated November 26, 1951

14. Technical Bulletin, Sequestrene, Alrose Chemical Company, Providence 1, R. I.

15. Technical Bulletin No. 2, "The Versenes", January, 1951, Bersworth Chemical Company, Framingham, Mass.