UNCLASSIFIED

XXXXXXXXXXXXXXXXXX

NYO-112(Del.)

AEC RESEARCH AND DEVELOPMENT REPORT

SURVEY OF PROCESSES
FOR
RADIUM RECOVERY
FROM
PITCHBLENDE ORES

By A. B. Babcock, Jr.

New York Operations Office
P. O. Box 30
Ansonia Station
New York 23, New York

Photostat Price $ 9.30
Microfilm Price $ 3.60

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

UNCLASSIFIED

DECLASSIFIED

NYO-112

SURVEY OF PROCESSES FOR RADIUM RECOVERY FROM PITCHBLENDE ORES

By A. B. Babcock, Jr.

ABSTRACT

This general report on radium summarizes the research work conducted by seven AEC contractors since 1943. The costs to concentrate and purify radium from refinery ore residues are discussed. Descriptions and flow sheets of several commercial processes are included to provide background information.

~~CONFIDENTIAL~~

TABLE OF CONTENTS

II. Background

III. Recent Research

VI. Appendix

A. Properties of Radium . . . .

B. Commercial Processes

~~CONFIDENTIAL~~

DECLASSIFIED

TABLE OF CONTENTS (continued)

I. Summary

For the last six or seven years the NYOO and its predecessor, the Madison Square Area of the Manhattan District, have been concerned from time to time with research on radium and its recovery from pitchblende ores. Most of this work was done because of the close association of radium with uranium in refinery processes and the necessity for fulfilling contractual agreements regarding radium recovery. During this period, much information and data have been accumulated.

This report has been written to summarize all the pertinent points of the radium research programs as well as the methods used in the commercial radium industry. The correspondence and library files of NYOO were reviewed, and problems of radium processing were discussed with several NYOO and contractor employees who have been closely associated with radium technology at one time or another.

The classical Curie procedure for radium recovery from pitchblende ores is substantially the same as the process used today by most radium producers. This process can be divided roughly into two stages: a chemical treatment to separate radium and barium from the bulk of the ore, and a fractional crystallization treatment to separate pure radium from the barium. The crystallization treatment is the only practicable method now known by industry for separating radium and barium on a production scale.

The research work at Yale University in 1944, proved that radium could be quantitatively retained in pitchblende ore digestion residues using any of three varied processes. The Mallinckrodt Chemical Works later developed one of these variations into what is now the standard process at the St. Louis refinery, in which radium is coprecipitated with the lead in the original ore and retained in the gangue residue. While this operation is well suited to uranium recovery, it would complicate subsequent radium recovery since the siliceous gangue would be bulky and difficult to handle in the alkaline solutions usually required in the commercial process.

Research work conducted in 1943 and 1944 at the Linde Air Products Company proved that the radium in relatively low grade pitchblende ores could be quantitatively retained in the residues of the sulfuric acid-sodium carbonate process for uranium recovery. During these same years, the University of Rochester showed that radium could be coprecipitated from nitric acid digestion solutions with the lead contained in most ores, thus eliminating the addition of barium salts as practiced in commercial processes.

To find a process for extracting radium from the present refinery residues, research work has been started by the Monsanto Chemical

Company at Mound Laboratory and at the Jersey City Laboratories of the Kellex Corporation. Since the work at each installation has been in progress for only a short time, no significant results have been obtained.

Ion exchange may develop to be one substitute for the classical fractional crystallization method for radium purification. Initial work on ion exchange was begun at Oak Ridge and is being continued by the Monsanto Chemical Company. The Kellex Corporation is investigating chemical methods, ion exchange, and other innovations such as chelation or chromatography, for radium purification.

In March 1949, the NYOO estimated costs for producing radium at the St. Louis refinery and at the Eldorado Gold Mines, Ltd. at Port Hope. Calculations indicated that radium would cost about \$1500 to \$2300 a gram at the St. Louis refinery, depending upon the production rate required. The costs at Eldorado were estimated at about \$3000 to \$3500 a gram. Neither of these estimates included the cost of the radium in the raw material.

II. Background

A. General

Early in 1948, the NYOO made several surveys on the procurement and availability of radium (Ref. 4e,g,k) at the request of Dr. J. B. Fisk, then the AEC's Director of Research. On June 4, 1948, Dr. Fisk asked the NYOO to maintain a continuing interest in the availability and location of radium (Ref. 4d), and since then several periodic reviews have been made on sources, stocks, prices (Ref. 4a,b,c,h,j), and economics for proposed plants. (Ref. 1c;2b,m;5a,c). This report, which is an extension of the original policy, has been written to summarize all previous AEC research on radium processing and to provide a brief description of the commercial radium industry.

B. Properties of Radium (Ref. 2c,g,l,o,p)

Radium, a member of the alkaline earth group (at. wt. 226), is a shining white metal which oxidizes rapidly in air and decomposes water. It is used, therefore, in the more stable salt forms. It has chemical properties very similar to barium, making it very difficult to separate the two elements. The chlorides of radium and barium are insoluble in concentrated acids, but soluble in water and dilute acids. The sulfates are insoluble in water and dilute acids, and only slightly soluble in concentrated acids. The carbonates are insoluble in water, but decompose in acids to the salt of the acid. Radium and barium can be separated because of the slight difference between the solubilities of their halides. The Curies first used this method of fractional crystallization to purify radium.

C. History of the Radium Industry (Ref. 2c,f,o,p;4c)

The Curies discovered radium in 1898. Its principal source is pitchblende which contains 257 milligrams of radium per short ton of U_3O_8, the equilibrium concentration. Significant amounts of radium are also found in the carnotite, torbernite, autunite, and betafite ores. The most important radium minerals are found in the Belgian Congo, Canada, United States, Czechoslovakia, Portugal, Madagascar, Russia, England, and Australia.

The first radium was produced from St. Joachimsthal (Czechoslovakia) pitchblende, the same deposits which the Curies used for their experimental work. Later, small deposits were found in England, Germany, the United States, Mexico, and the Indies, but were exploited for only a short time. In 1911, large deposits of carnotite were found in the United States, and by 1913, several U. S. companies were producing radium commercially. Until 1922, the United States produced about 80% of the world's supply of radium. However, because of the discovery in 1913 and subsequent exploitation in 1922 of the rich pitchblende deposits in the Belgian Congo, the Union Miniere du Haut Katanga dominated the world market within a few years. Pitchblende deposits discovered in 1929 at Great Bear Lake have enabled the Canadians to compete to some extent with the Belgians. Radium prices had fluctuated greatly for more than 30 years, but in 1937, an agreement between the Union Miniere and Eldorado Gold Mines, Ltd. established the price of radium. For the last ten years, the demand for radium has been relatively low so that neither the Belgians nor the Canadians have recently been producing at their full plant capacities of about 15 and 10 grams per month respectively. Union Miniere stated recently (Ref. 41) that it can increase its production to about 30 grams per month on about three months' notice.

D. Typical Commercial Process (Ref. 2)

Most commercial producers still use the Curie process or some of its variations to extract radium from pitchblende ores. This process is divided into two stages: first, a chemical treatment to concentrate the radium as a radium-barium sulfate cake, and secondly, the separation of the radium from barium by fractional crystallization.

In the first stage, the ore is generally treated with a barium salt and sulfuric acid to solubilize the uranium, iron, copper, etc., and to leave a residue containing gangue and barium, radium, and lead sulfates. This residue is treated with sodium chloride to remove lead and then digested with sodium carbonate to convert radium and barium to the carbonates which are soluble in hydrochloric acid. The acid treatment removes the insoluble silica, leaving an impure radium-barium chloride solution. Repeated treatments with sulfuric acid, sodium carbonate and hydrochloric acid purify the radium-barium mixture which is finally sent to the second stage.

The fractional crystallization stage depends upon the small differences between the solubilities of the radium and barium chlorides or bromides. The process is tedious and requires many crystallizations and recombinations of liquid and solid fractions of similar concentration. Radium bromide over 95% pure is finally dried and tubed or converted to other compounds as required.

E. Uses of Radium (Ref. 4a,c[redacted]

The principal use for [redacted]um outside of AEC is for the treatment of cancer. The present world stock of medical radium is estimated at about 550 grams, while the radium used for radiographic purposes (examinations of castings, etc.) is estimated at about 75 grams. Small amounts of radium are used by the luminescent industry (about 20 grams per year), although its use in the latter field is decreasing due to the substitution of mesothorium. The radium in medical and radiographic uses is in a recoverable state, but the luminescent radium is generally considered unrecoverable.

III. Recent Research

A. Yale University (Details in Appendix) (Ref. 1h,i,l-p,t)

In 1944, Yale University began research to find a good method for refining uranium from pitchblende ores. Secondary objectives of this work, under the direction of Dr. H. S. Harned, were to find a satisfactory way to separate uranium from radium in the refining process which would recover as much radium as possible, and to find a process by which subsequent recovery of radium might be simplified compared to the usual commercial processes.

These secondary objectives were important since only the uranium in foreign ores had been purchased. If radium were lost when the ore was refined, the Manhattan District was committed to pay a penalty to the ore supplier. Also, uncontrolled radium could seriously contaminate the uranium products or refinery process equipment, and might present difficult health problems.

The simplification of the radium recovery process was of long range importance. If radium were to be recovered eventually from the ores, the minute quantities of radium should logically be separated from the bulk of the gangue residues by the ore digestion operation. Such a process would be of tremendous economic importance in the refining of radium.

The Yale group studied three separate processes, commonly known as the "one-step", "two-step", and "three-step" processes, for the initial digestion of the pitchblende ore. With its variations, each process had its own merits and disadvantages, although a "two-step" process was eventually developed for the St. Louis refinery.

In the "one-step" process, the ore was treated with nitric and sulfuric acids to dissolve the uranium. After acid digestion, a barium salt was added to remove the excess sulfate ion and the radium by coprecipitating it as barium-radium sulfate. The mixture was then further digested and filtered hot, leaving the gangue and insoluble sulfates in the residue filter cake. The filtrate was processed for the uranium, and the cake was stored for eventual radium recovery.

In this process, the uranium recovery was about 99%, and the retention of radium in the residue was also about 99%. The filtration characteristics of the slurry were good providing ore was added to a hot acid solution rather than the reverse.

The "two-step" process utilized the lead in the original ore to coprecipitate radium, instead of using barium salts as in the "one-step" procedure. After digestion of the ore with nitric acid, sulfate ion was added as sodium sulfate or sulfuric acid. The lead in the ore was precipitated as lead sulfate, at the same time bringing down the radium as a sulfate. The mixture was filtered to separate a gangue-lead-radium cake from the uranium solution. Excess sulfate ion, which could interfere in later organic extraction steps, was removed from the filtrate by the addition of barium carbonate. In this process, the separation efficiency of radium from uranium was about 99% but filtration characteristics were generally poor.

The "three-step" process held promise of becoming important if radium refining were desired since it would permit the radium to be easily separated from the gangue as a lead-radium cake containing little barium (only that contained in the original ore). The ore was digested with nitric acid as with the other methods, but the slurry was filtered before the addition of any sulfate ion. In this way, the gangue was separated immediately from both radium and uranium. Sulfuric acid was added to the filtrate, precipitating lead and radium sulfates as before. The lead, radium, and the original barium were separated from the uranium by filtration, and barium carbonate was added to the filtrate to remove the excess sulfate ion. Analyses on the second and third filtrates indicated that 98-99% of the original radium was precipitated in the lead cake.

The "three-step" process, while having many advantages, could cause a large proportion of radium to precipitate in the gangue residues if the sulfur content of the original ore were high. In such cases, the sulfides in the ore would oxidize to sulfates when treated with nitric acid. If these sulfates were soluble under digestion conditions, the radium would precipitate as the sulfate. Therefore, either low sulfide ores must be used in this process or the sulfur content must be reduced prior to the initial digestion.

In general, the radium recovery was influenced by the type of ore, the digestion time, and the concentration of excess nitrates. One of the most important results was that lead sulfate could coprecipitate radium as efficiently as barium. This was significant since lead can be easily separated chemically from the radium sulfate, leaving a radium-barium mixture (barium from original ore) with a much lower barium to radium ratio than is ordinarily possible in commercial processes. Therefore, the coprecipitation of radium with lead sulfate could reduce the number of radium and barium separations required by the fractional crystallization procedure.

The Yale group also did some preliminary work on the separation of lead from the lead-barium-radium sulfate cake of the "three-step" process. The cake was treated with sodium bicarbonate at room temperature to convert only the lead sulfate to the carbonate. The slurry was filtered, and the residue was digested with nitric acid to form soluble lead nitrate. The barium-radium sulfate cake contained about 60-80% of the original radium.

When the lead sulfate cake was slurried in hot ammonium acetate solution, virtually all the lead dissolved, leaving a barium-radium sulfate cake with about 95% of the original radium. When the ammonium acetate digestion was performed at room temperature, only about 50% of the radium was recovered in the barium-radium cake.

Finally, a sodium hydroxide treatment was investigated. The lead cake was digested with sodium hydroxide, and the resulting slurry was filtered, leaving about 50% of the original radium in the barium-radium cake. In this process, the lead sulfate was separated because of its solubility in strong alkaline solution.

Dr. Harned's group also worked on some phases of the analytical problems of radium. The analytical procedures developed were designed to give fairly accurate results with a minimum of time and effort. One procedure was designed for residues containing large amounts of sulfates and small amounts of radium. Results varied considerably among different operators, but were satisfactorily consistent when performed by the same operator. The second procedure was for residues containing small amounts of both sulfate and radium (about 2% of that in the original ore). The average error of this procedure was about ±7%, and the larger errors were possible due to the small sample size. However, the results were sufficiently accurate for the estimation of undissolved radium when they were based upon the original radium in the ore.

B. University of Rochester (Details in Appendix) (Ref. 1g)

In 1943 and 1944, at the University of Rochester, Dr. J. F. Flagg directed a group which made a study of the optimum conditions for recovering radium from ore extracts by coprecipitation with lead sulfate. The Manhattan District also desired information on whether the average ore contained sufficient lead to coprecipitate the radium, the completeness of the coprecipitation, and how variations in the lead precipitation conditions would affect the percent radium retention.

The Rochester group experimented on a solution, obtained from the nitric acid digestion of a high grade pitchblende ore, which was similar to the digestion solution obtained by the Yale "three-step" process. When the liquors were added to known amounts of sulfuric acid or ammonium sulfate solutions, lead and radium sulfates precipitated. The filtrates were analyzed for radium.

Results showed that the mol ratio of sulfate to lead could be varied from 3 to 40, with other conditions except acid concentration held as constant as possible, without appreciably affecting the per cent of the radium precipitated, although a slight improvement was noted with increasing ratios. In twelve experiments, the per cent retention was within the range of 99.50% to 99.98%.

High temperatures during precipitation were shown in two tests to lower somewhat the per cent retention. In one experiment at 25°C, the retention was 99.89%, while in the other performed at 100°C the retention was 98.13%.

The aging time of the slurry following precipitation was shown to have little effect upon the radium retention. Three experiments in which the aging time was varied from 15 minutes to 18 hours indicated a difference in retention of only 0.01%.

The ratio of lead to radium, when increased about 150-fold, improved the per cent retention slightly, other conditions being held as constant as possible. In five tests, the retention was within the range of 98.60% to 99.92%.

The solubility of lead sulfate was found to increase with increasing nitric acid concentration, even when excess sulfuric acid was present, and at constant temperature the solubility depended upon both the nitric and sulfuric acid concentrations. Other tests showed that the use of ammonium sulfate in place of sulfuric acid, or the use of alcohol in an attempt to reduce the solubility of lead sulfate, offered no advantage.

The work at Rochester proved that the lead which occurs naturally in the pitchblende ores is sufficient to coprecipitate over 99% of the radium under the conditions of the process.

C. Mallinckrodt Chemical Works (Details in Appendix) (Ref. 1k,t)

The development work performed at the Mallinckrodt Chemical Works extended the Yale studies and was designed to dissolve the maximum amount of uranium from the ore with a minimum amount of radium contamination. The applicability of the process to full scale production was of prime importance. Mallinckrodt did no work on the Yale "three-step" method because the pressure to complete the uranium refining process in the shortest possible time would not permit the development of a practicable plant-scale scheme to obtain radium free from gangue. However, six principal variations of the Yale "one-step" and "two-step" processes were investigated.

Process A was essentially the "two-step" process in which the ore was suspended in hot water. An excess of nitric acid was added to the slurry, followed by the addition of sulfuric acid. Filtrate analyses showed that an average of 99.8% of the original radium had been coprecipitated with the lead sulfate, and that a maximum of 0.3% of the radium was lost to the filtrate. The filtration characteristics, however, were poor.

Process B was very similar to the Yale "one-step" process. The ground ore was digested as above, but then barium carbonate was added, forming barium nitrate in solution. Next, sulfuric acid was added to precipitate the lead, barium, and radium sulfates which were removed along with the gangue upon filtration. In six tests of this process, the average loss of radium was 0.78% of the total, although one loss was as high as 2%. The sulfuric acid consumption was about half of that in "A", and the slurry was again difficult to filter.

In order to improve the filtration characteristics of the above process slurries, the ore was added to a hot acid mixture. The rest of Process C was similar to "B" above. Four tests of this procedure showed an average loss of 1% of the original radium, but slurry filtering was improved.

Developments indicated that the extraction of uranium could be improved if sulfuric acid were added to the digestion mixture before the barium. Therefore, Process D was identical to the Yale "one-step" process. It should be mentioned that the addition of barium carbonate was better than barium nitrate since the amount of nitric acid required to convert the carbonate to the nitrate could be added to the digestion mixture at the start, thereby gaining the advantage of slightly higher acid concentrations. Four tests of this process showed an average of 99.07% radium retention, with a maximum loss of 2.04% and a minimum loss of 0.07%.

The addition of barium was omitted in Process E since Mallinckrodt thought its use might interfere with the dissolution of the uranium or with the retention of the radium in the residues. The process was similar to "D" except for the barium omission. An average of 0.56% of the radium was lost to the filtrate in six tests, with a maximum loss of 1.3%.

Finally, in Process F, the nitric and sulfuric acids were mixed and heated before the ore was added, and the barium was omitted. In two tests, an average of 0.33% of the original radium remained in the filtrate when a 79% U_3O_8 ore was used. Filtration characteristics were good.

From a study of the variables in the processes above, the Mallinckrodt Chemical Works concluded that: (1) ore, ground so that 65-70% passed through 50 mesh, was sufficiently fine; (2) filtration and washing were more rapid when ore was added to acid, rather than the reverse; (3) while the uranium recovery was generally good, best results were obtained when the nitric and sulfuric acids were mixed before the addition of the ore; (4) the acid concentrations did not significantly affect the radium recovery; (5) the addition of barium was not needed to coprecipitate radium under the conditions studied; and (6) uranium could be extracted efficiently on a plant scale from ores containing between 40 and 67% uranium, leaving a gangue-lead residue containing about 99.5% of the original radium. Occasional radium losses to the filtrate might be as high as 1.5%.

Mallinckrodt ran pilot plant tests based on the results of the laboratory work above. The final procedure developed for the production plant was very similar to Process F above and is described in detail in the Appendix.

Production operations for over five years at the ore refinery in St. Louis have proved that for all practical purposes the radium is quantitatively retained in the digestion residues. In addition, the operation for about two years of the C-3 Process for the recovery of small amounts of uranium from the digestion residues has proved that the radium solubility is not affected by the alkaline carbonate treatment of the process.

D. Linde Air Products Company (Details in Appendix) (Ref. 1s,t,2b)

When the sulfuric acid process for relatively low grade pitchblende ores was in the development stages, Linde made several laboratory and pilot plant experiments to insure the quantitative retention of radium in the digestion residues. In one experiment, the ore was digested in 50% sulfuric acid with small amounts of nitric acid or sodium chlorate as an oxidizing agent and a small amount of barium chloride to aid the coprecipitation of the radium. In twelve experiments, an average of considerably less than 0.01% of the radium was lost to the filtrates.

In another experiment like the proposed plant procedure, the ore was digested with sulfuric acid and manganese dioxide or nitric acid was added to oxidize tetravalent uranium. Barium chloride was added to coprecipitate radium. After digestion, the mixture was treated with sodium carbonate to precipitate impurities, such as iron and aluminum, and then filtered. In eight tests, an average of about 0.01% of the original radium was in the filtrate.

These laboratory experiments indicated that the chances were slight for any appreciable amount of radium to be lost in the alkaline filtrates. Also, the sulfuric acid concentration, the pH of the alkaline solution, and the oxidizing agents did not seem to affect the efficiency of the radium retention. Subsequent pilot plant tests using the proposed plant procedure proved that 99.9% or more of the original radium would be retained in the digestion residues. In one run, the amount of barium chloride was reduced considerably without any apparent effect upon the radium retention.

Production at Linde for about a year and a half on several grades of pitchblende ore verified the laboratory and pilot plant results. Radium was quantitatively retained in the ore residues throughout the acid and carbonate treatments.

E. Dayton Area (Details in Appendix) (Ref. 1a,i)

Late in 1949, the Monsanto Chemical Company began research work at the Mound Laboratory, Miamisburg, Ohio (Dayton Area) on the concentration and purification of radium from refinery residues. Monsanto has been developing a hydrofluoric acid method for removing silica from the Mallinckrodt digestion residues before the radium and barium are extracted by repeated sodium carbonate and acid treatments. In the course of the work, Monsanto has determined that unless silica is removed early in the process, the residues will form a slimy, unfilterable mass upon alkaline digestion. When the silica is removed as gaseous silicon tetrafluoride, however, no further filtration problems arise.

Recently, Monsanto began preliminary work on the ion exchange process for radium and barium separation, first checking the work done by Tompkins at Oak Ridge. (See III-F). The use of Dowex 50 resin with a synthetic solution, containing microgram quantities of radium, indicates that fairly good separation of the two elements can be obtained.

F. Ion Exchange Studies (Details in Appendix) (Ref. 1d,e,f,l,q,r)

The idea of using ion exchange for the separation of barium and radium, instead of the classical fractional crystallization procedure, is relatively new in the history of radium recovery processes. In 1947, Dr. E. R. Tompkins at Oak Ridge National Laboratory, in the course of his investigation of ion exchange processes on fission products, found that barium and strontium in low concentrations could be separated effectively by using an Amberlite cation resin. When Dowex 50 (a new resin) proved even more effective for this work, Dr. Tompkins thought that it might well be applied to the separation of barium and radium.

Additional experiments with Dowex 50 showed that barium, radium, and strontium in trace quantities could be separated quite sharply upon elution of the resin. Dr. Tompkins concluded that barium could probably be separated from radium much more easily on a commercial scale by this ion exchange method than by fractional crystallization. Also, ion exchange could probably be adapted more easily to remote control. While Dr. Tompkins did not investigate the use of the ion exchange for quantitative analyses, he believed that it might be applicable.

Recently the Oak Ridge National Laboratory has done a great deal of work on the "RaLa Process" for separating Barium-140 from lead and other impurities by ion exchange in combination with chelation. This process may help solve some of the ion exchange problems of radium and barium separation since it deals with elements which are chemically very similar to radium. OK

G. Kellex Corporation (Ref. 1b,d,e,f)

In March 1950, the NYOO expanded an existing research contract with the Kellex Corporation to include a radium concentration and purification program. (This work on residues from the St. Louis refinery supplements that being conducted at Mound Laboratory.) Work has begun on a scheme to remove the lead, barium, and radium sulfates from the residue by treatment with concentrated sulfuric acid, or even with fuming sulfuric acid. These sulfates ordinarily are slightly soluble in concentrated acid, but can be precipitated from solution upon dilution. Therefore, if the sulfates can be dissolved under the proper conditions and reprecipitated after filtering out the gangue, considerable bulk could be eliminated early in the process.

Kellex has started to investigate the use of Versene and sodium polyphosphate for removing lead, barium or radium sulfates from the refinery residues. The ORNL, while working on the RaLa Process, has studied to some extent the ability of Versene to dissolve lead and barium sulfates. If Versene or the polyphosphate could remove these sulfates from the bulk of the residues, the complicated chemical treatment for concentrating radium would be eliminated. OK

Kellex may also investigate some of the other possible methods to remove radium and barium sulfates from the bulk of the K-65, such as: metathesis of the sulfates by alkali metal carbonates; reduction to sulfides and conversion to water soluble salts; conversion to halides by treatment with ammonium halides; conversion to chlorides by treatment with carbon dioxide and chloroform; reduction and halogenation to chlorides by the reaction of carbon and chlorine; flotation of the sulfates; and several other less promising chemical transformations.

Kellex may study the possibility of using the Yale "three-step process as a standard refinery procedure. If the difficulties of poor filtration characteristics and the relatively high reagent usage of this process can be overcome, radium recovery in a new plant might be greatly simplified. Research of this nature will parallel similar work on new uranium refining techniques on which Kellex is presently engaged.

In the Kellex program, experimental work on the final purification step will probably include studies of ion exchange, chelation, extraction, precipitation, and chromatographic methods.

IV. Production Costs (Details in Appendix) (Ref. 5)

In February, 1949, the NYOO was asked (5d) to prepare a rough estimate of the cost for building and operating a plant at the St. Louis refinery to produce radium [redacted] These cost estimates (5c) were based on the following assumptions: the Yale "three-step" process would be used to provide a relatively pure lead-barium-radium cake; 95% of the radium would be recovered at a purity of 95% or better; contractual obligations of the AEC to African Metals Corporation (and the cost of the radium in the ore) were not considered; and the space required for enlargement or construction of the plant would be available at the St. Louis refinery.

[redacted]

V. Conclusions

The properties of barium and radium are relatively simple and have been known for many years. Any great improvement in the recovery and purification of radium will probably be made only through successful application of new techniques or previously untried methods used in other industries. It follows, therefore, that considerable research will be required to reduce the costs of proved commercial processes.

Future radium research should be directed toward two goals; first, finding a workable method to extract radium efficiently from refinery residues (with costs important, but still secondary), and secondly, developing a method to extract and purify radium more inexpensively than can be done by commercial methods.

The earlier research work by contractors of the Madison Square Area (Yale, Mallinckrodt, Linde, Rochester) is important because it provides basic data on the behavior of radium, lead, and barium during the digestion of pitchblende ores. Any radium research program would be a natural expansion of this earlier work and must necessarily be an integral part of a general research contract on new uranium refining techniques since the behavior of radium must be known whether the operation of radium recovery plant is planned or not.

No definite conclusions can be drawn at this time about most promising methods for extracting radium from refinery residues. Ordinary chemical methods appear to be the only solution to the problems of the initial stages of the process, and future research will probably be, to some extent, a matter of trial and error to find the most efficient and economical process.

At present, ion exchange techniques seem to be the best substitute for the tedious fractional crystallization method for separating radium from barium.

Also, costs for the concentration and purification of radium probably cannot be determined accurately now. There are so many unknown variables in the calculations, such as the cost of the raw material, the possibility of new processes as a result of research, the reagents required by the refinery residues, and ore contract negotiations, that processing costs probably will not be known any more accurately until more definite research and contract information is obtained.

[redacted]

VI. Appendix

[redacted]

[redacted]

A. Properties of Radium (from miscellaneous sources)

1. Atomic Properties:

Atomic Weight - 226.05
Atomic Number - 88
Valence State - 2

Decay Series:	Uranium(238)Radium Half life: 1590 years Radiation: alpha (4.79 mev), gamma (0.19 mev)
Isotopes:	At. wt. 223, 224, 225, 226, 228

2. Comparison of radium and barium compounds:

	Specific Gravity (g./cc)		Melting Point °C		Solubility (g./100 ml.)	
	Ra	Ba	Ra	Ba	Ra	Ba
Bromide	5.79	4.78	728 900 subl.	847 d.	70 (20°C)	98 (0°C) 149 (100°C)
Chloride	4.91	3.86	1000	925	25 (cold)	31 (0°C) 59 (100°C)
Sulfate		4.50		1580	2×10^{-6}(25°C) 5×10^{-6}(45°C)	2.3×10^{-4}(45°C) 3.9×10^{-4}(100°C)
Iodate		4.99			0.0175(0°C) 0.170(100°C)	0.022(cold) 0.2(100°C)
Metal	5 (?)	3.5	960 1140(t.p.)	850 1140(t.p.)		

(In 3% HCl, $BaSO_4$ sol. = 0.006)

3. Radium Conversion Factors

	Mol.Wt.	Ra	$RaBr_2$	$RaBr_2 \cdot 2H_2O$	$RaCl_2$	$RaCl_2 \cdot 2H_2O$	$RaCO_3$	$RaSO_4$
Ra (element)	226.05	1.0000	1.7073	1.8666	1.3138	1.4732	1.2655	1.4250
$RaBr_2$	385.88	0.5857	1.0000	1.0934	0.7695	0.8629	0.7412	0.8347
$RaBr_2 \cdot 2H_2O$	421.91	0.5357	0.9146	1.0000	0.7038	0.7893	0.6779	0.7634
$RaCl_2$	296.96	0.7612	1.2995	1.4208	1.0000	1.1213	0.9633	1.0847
$RaCl_2 \cdot 2H_2O$	333.00	0.6788	1.1588	1.2671	0.8918	1.0000	0.8590	0.9673
$RaCO_3$	286.06	0.7902	1.3491	1.4750	1.0382	1.1641	1.0000	1.1261
$RaSO_4$	322.11	0.7017	1.1980	1.3099	0.9219	1.0338	0.8880	1.0000

4. Radiation Absorption (for radium and daughter products):

Range of alpha rays in air (S.T.P.) - 3.21 cm.
Alphas completely absorbed by - 0.006 cm. Al fail
Hard beta rays completely absorbed by - 2 mm. lead
Hard beta rays half absorbed by - 0.1 mm. lead
Hard gamma rays half absorbed by - 14 mm. lead

B. Commercial Processes

1. Fractional Crystallization Procedure (Quoted from Ref. 2j)

The radium-barium sulfate concentrates are transferred from the plant to the laboratory, where they are changed to carbonates by boiling with soda ash in steel kettles. After filtration and washing, the carbonates are acidified with hydrobromic acid, and the bromide liquors are purified for removal of the lead, iron, copper, etc., using barium hydroxide and barium sulfide as purifying agents. All impurities and insoluble residues are collected, and when a certain quantity has accumulated, they are treated again with sulfuric acid, soda ash, and hydrobromic acid, and the purified solution added to the bromide liquor already available. The final residue still carries a little radium; it is therefore sent back to the leachers at the commencement of the wet process.

The separation of the radium from the barium is made by the crystallized fractioning process, using the difference of solubility of the radium and the barium in water. The purified bromide liquors are evaporated to saturation and allowed to cool. A crop of crystals comes out in the bottom, richer in radium and poorer in barium than the liquor above it. The operation is repeated separately on the crystals and on the solution in a system of quartz basins and monel metal pails to insure an even flow of successively richer and richer radium bromide in the crystals, and poorer and poorer barium bromide in the liquors. (See Fig. 1.) The initial solution of bromide has a ratio of about one part radium to 400,000 parts of barium. The head crystals, after about ten crystallizations, show about one part of radium to about 600 of barium. These crystals are separated from the system, and accumulated for about one month. They are then repurified in the same way as the original liquor, and the crystallization recommenced and carried to a point where the ratio is nine parts of radium to one of barium. They are then dried, transferred into glass tubes and sealed therein by a blowtorch.

The waste liquor of barium bromide is exhausted from the fractioning process when it shows a radium content 2 x 10^{-5} mg. of radium per liter. It is used to regenerate the hydrobromic acid by precipitation with sulfuric acid and evaporation of the solution on a water bath.

(Retreatment of residues is not considered economical or practicable when the radium content is 3 mg. per ton. Radium losses are mainly in waste liquors from NaOH and carbonate treatments. All solutions are tested before being discarded. $BaCl_2$ is added to sump waters and used for barium supply. Overall radium recovery is 90% or better.)

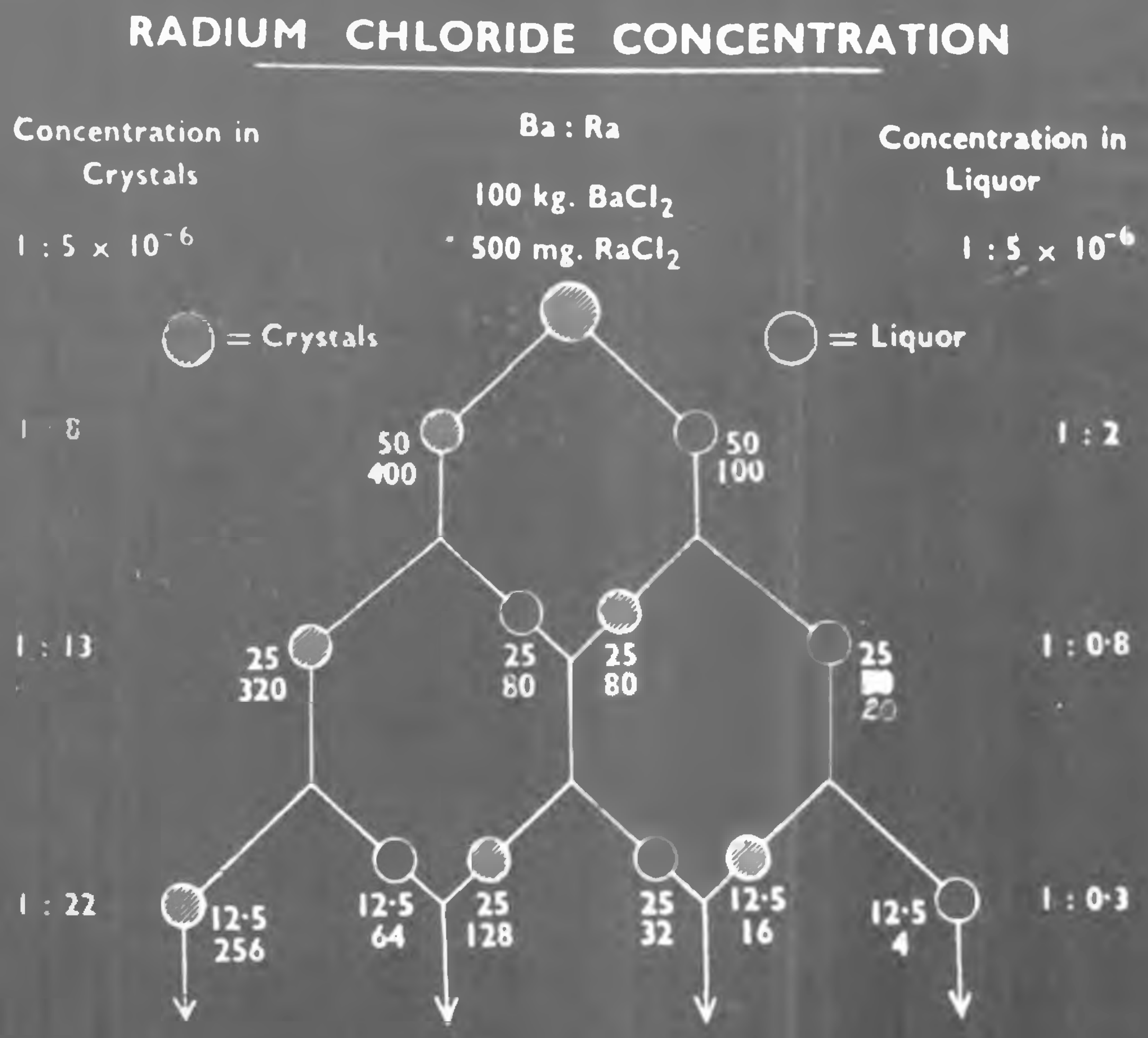

RADIUM CHLORIDE CONCENTRATION
Concentration in Crystals
Ba : Ra
Concentration in Liquor
100 kg. $BaCl_2$
500 mg. $RaCl_2$
1 : 5 x 10^{-6}
1 : 5 x 10^{-6}
= Crystals
= Liquor
1 : 8
50
400
50
100
1 : 2
1 : 13
25
320
25
80
25
80
25
20
1 : 0·8
1 : 22
12·5
256
12·5
64
25
128
25
32
12·5
16
12·5
4
1 : 0·3

FIG. 1

ST. JOACHIMSTHAL

Flow Sheet

FIG. 2

GREAT BEAR LAKE MILL
Flow Sheet

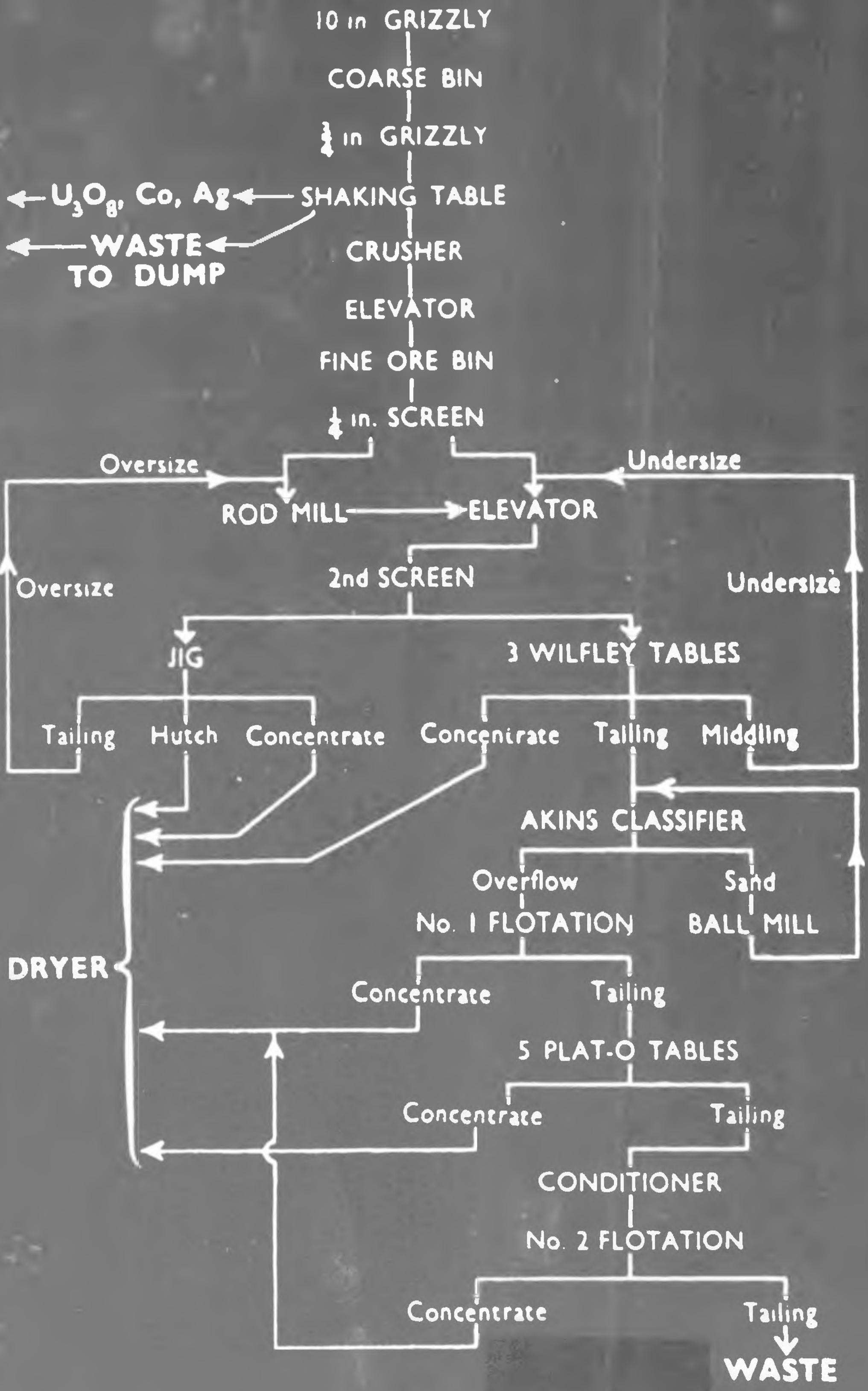


FIG. 3

PORT HOPE (ONTARIO) REFINERY

Flow Sheet

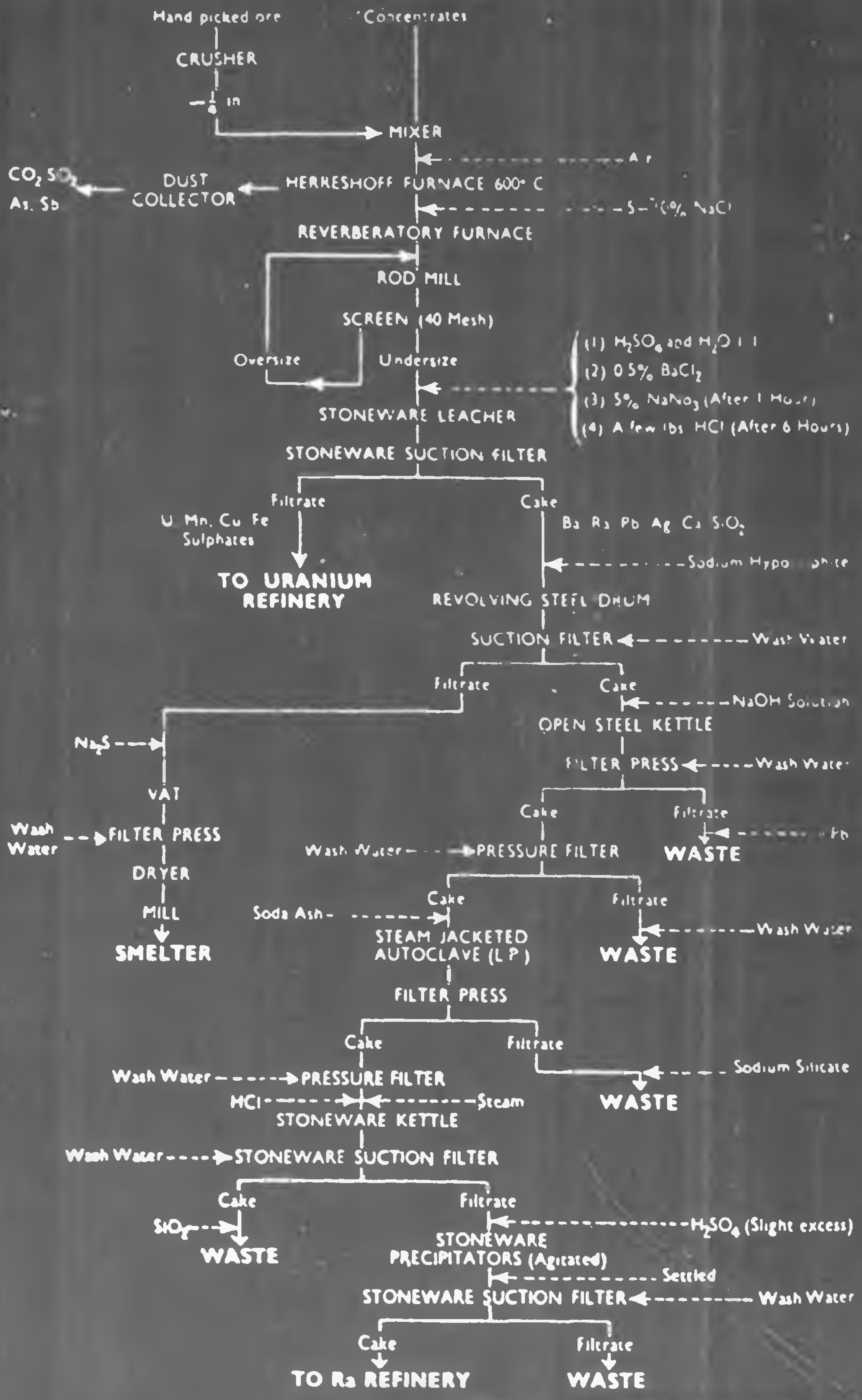


Fig. 4

PORT HOPE (ONTARIO) REFINERY

Ra Ba Separation

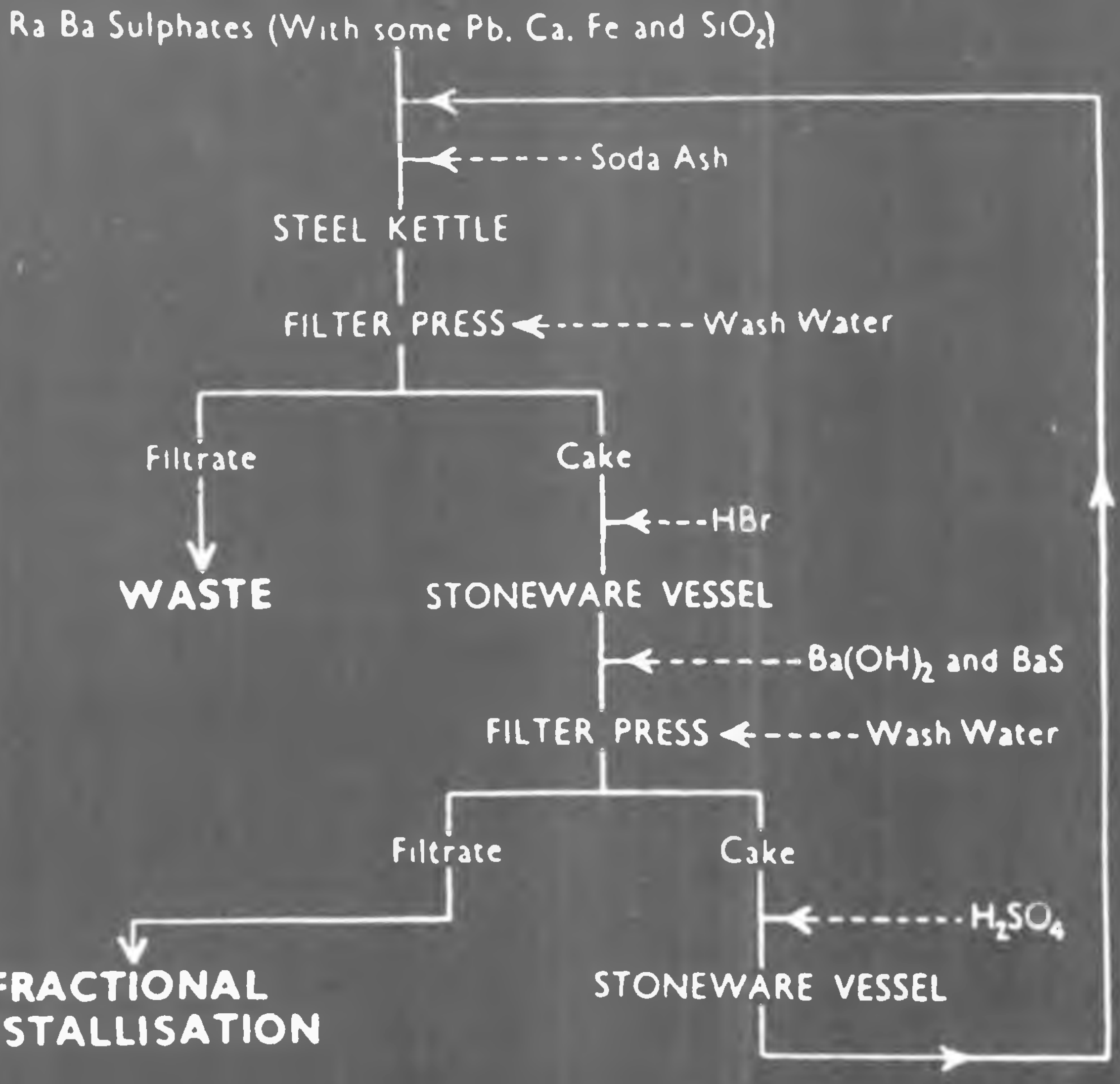
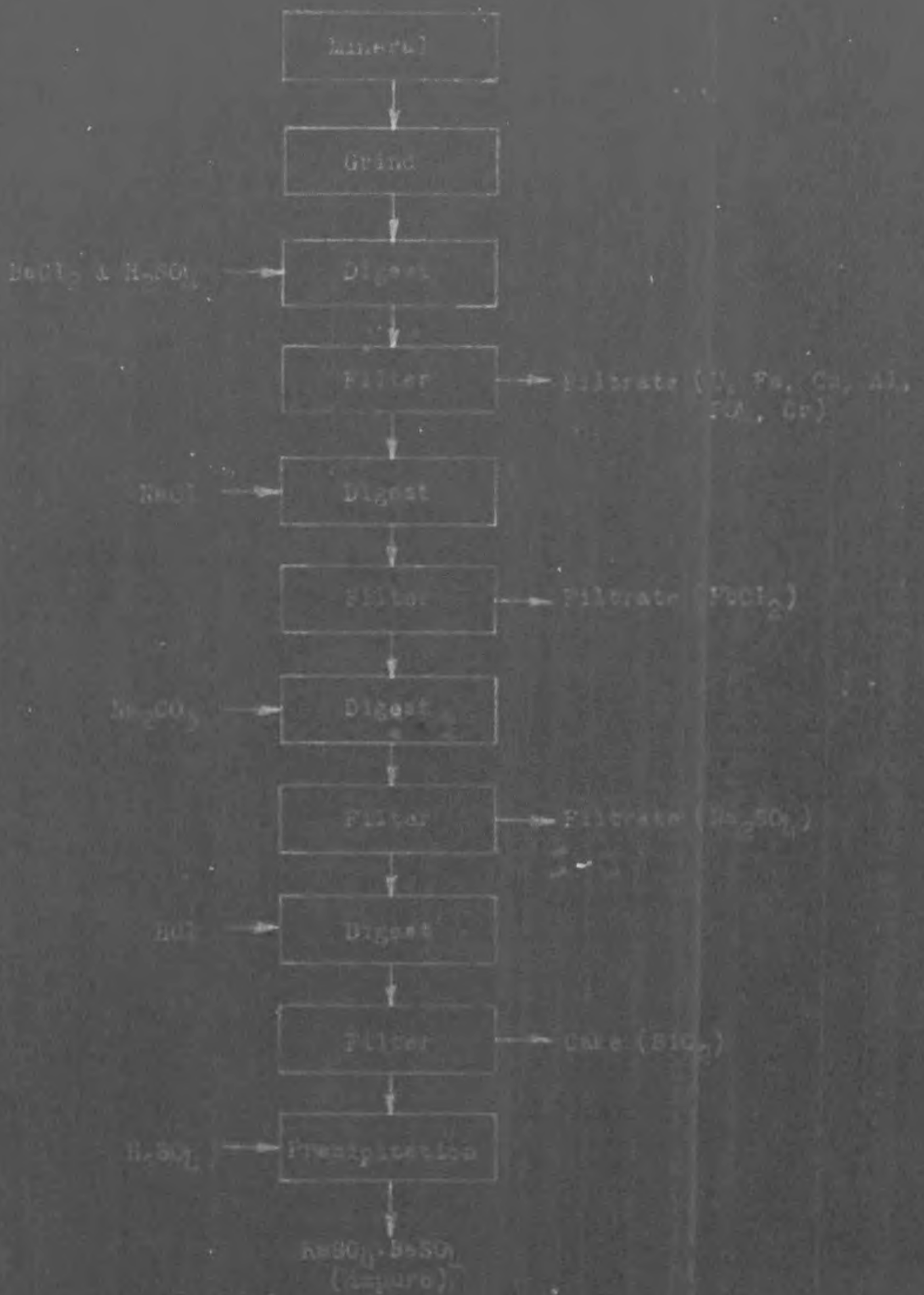


Fig. 5

UNION MINIERE
DU HAUT KATANGA

Radium Plant Flow Sheet



(Remainder of process similar
to Port Hope Process)

C. Research Details

1. Yale University (From Yale research references)

a. Raw Materials: The following analysis, made by the U. S. Bureau of Standards, may be considered fairly representative of all the ore used in the Yale work. (Only part of analysis reported here.)

U_3O_8 - 69.02%
PbO - 6.09
SO_3 - 1.27
SiO_2 - 10.5
Fe_2O_3 - 0.94
Al_2O_3 - 1.53
CaO - 2.2
MgO - 0.9
H_2O - 2.5
CO_2 - 0.6

(Ra in all work: input per experiment = 1.74×10^{-5} g.)

b. "One-Step" Procedure:

Time (min.)	Operation
0	100 g. ore slurried with water, and HNO_3 added slowly. In 1.3 times theoretical digestions, 43 ml. of 69.5% acid required. Water for slurrying also 43 ml.
3	HNO_3 addition complete. Mixture stirred at 95-100°C.
13	50 ml. boiling water usually added to aid stirring and to compensate for evaporation losses.
33	Digestion ended. (All experiments reported used 30 min. digestion period which was sufficient to remove all U from ore and may have prevented other constituents from dissolving.) Slurry diluted, usually to 200 ml., with boiling water.
35	H_2SO_4, diluted 1:1 with water, added.
37	Addition of $BaCO_3$ slurry begun.
40	$BaCO_3$ addition completed. Mixture kept at 95-100°C. for 30 min.
70	Mixture filtered at 95°C. Cake washed free of U. Radium assays on filtrate made.

c. Results from Above Procedure:

Exp. No.	HNO_3 used X theo.	ml. of Slurry	g. of H_2SO_4	g. of $BaCO_3$	g. Ra in filt. x10-5	% Ra in Cake
D11	1.5	200	15	30	0.055	96.8
D12	1.3	200	15	27	0.020	98.85
D13	1.3	100	15	27	0.021	98.8
D14	1.3	200	9.5	16	0.049	97.2
D18A	1.3	200	4.7	10	0.390	77.6
D18B	1.3	200	4.7	10	0.396	77.2
D19*	1.3	200	4.7	10	0.361	79.2
D21**	1.3	200	4.7	10	0.270	84.5
D22***	1.3	200	4.7	10	0.156	91.0
D23	1.3	200	4.7	10	0.450	74.2
D24	1.3	200	4.7	10	0.380	78.2
D25	1.3	200	4.7	10	0.406	76.6
D26***	1.3	200	4.7	10	0.284	83.7

* $BaCO_3$ added to slurry at boiling point.
** Mixture filtered at 50°C.
*** Final slurry digested for 4 hrs. at 95-100°C. before filtration.

i. Experiments D11 to D14 designed to precipitate all the Pb from solution, then precipitate the excess sulfate with $BaCO_3$. This gave high Ba in cake, with the Ba-Ra ratio about 1,000,000 to 1.

ii. Experiments D18A to D26 designed so H_2SO_4 and SO_3 in ore were stoichiometric with $BaCO_3$ added, giving a Ba-Ra ratio of 400,000 to 1.

iii. Radium analyses on filtrates: standard $BaSO_4$ pptn--Na_2CO_3 fusion method. The percentage Ra in cake found by difference.

iv. (Filtration rates and other data given in the original work.)

d. Modified "One-Step" Procedure:

Time	Operation
0-13	(Same as original procedure.)
33	Digestion ended. Mixture diluted to 200 ml. with hot soln. containing 13.2 g. $Ba(NO_3)_2$, corresponding to a Ba-Ra ratio of 400,000:1.
35	H_2SO_4, diluted 1:1 with water, or Na_2SO_4 soln., added to mixture. Mixture stirred 15 min. at 95-100°C.
50	(Same as original.)

e. Summary of Results of Modified Procedure:

Exp.No.	g. Sulfate added	Sulfate Equiv.to*	ml. of Filtrate	g. Ra x10-5 in filtrate	% Ra in Cake
D27	7.7 H_2SO_4	Pb + Ba	125	0.0164	99.05
D28**	" "	"	147	0.0035	99.80
D33	" "	"	148	0.0166	99.05
D34	" "	"	134	0.0130	99.25
D35***	" "	"	132	0.0110	99.35
D36***	" "	"	112	0.0115	99.35
D44	4.95 "	Ba	117	0.119	93.15
D45	" "	"	128	0.186	89.3
D46	7.2 Na_2SO_4	"	132	0.266	84.7
D47	" "	"	132	0.234	86.5
D48	11.1 "	Pb + Ba	142	0.0234	98.65

* Assumes all Pb in ore found in solution.
** Soln. cooled to 25°C before filtration.
*** $Ba(NO_3)_2$ formed by simultaneous addition of 10 g. $BaCO_3$ and 6.5 ml. 69.5% HNO_3 to reaction mixture.
All above experiments used 1.3 times theoretical HNO_3.

f. "Two-Step" Procedure:

Time	Operation
0-13	(Same as "one-step")
33	Digestion ended. Slurry diluted to 200 ml. with hot water, and Na_2SO_4 added slowly until all Pb precipitated (22.6 g. Na_2SO_4). Mixture digested 30 min. at 95-100°C.
63	Filtered at 95°C. Cake washed free of U. Ra assays made on filtrate.

g. Results of "Two-Step" Process:

Exp.No.	ml. of filtrate	g. Ra in filtrate x10-9	% Ra in Cake
D40	116	7.7	99.96
D41	126	23.0	99.87

h. "Three-Step" Procedure:

Time	Operation
0	100 g. standard ore slurried in 43 ml. water. 43 ml. of 69.5% HNO_3 (1.3 x theo.) added slowly.
3	All HNO_3 added. Stirring at 95-100°C begun.
13	50 ml. hot water added to facilitate stirring and offset evaporation losses.
33	Digestion ended. Mixture was diluted to either 150 ml. or 200 ml. with hot water and filtered hot.
(45)	Gangue cake washed with 1-50 ml. hot water (displacement), reslurried with 150 ml. hot water, and given 2 washes with 50 ml. hot water.
(65)	Filtrates cooled to room temperature and 12.2 g. H_2SO_4, diluted 1:1, added slowly with stirring. (Pb precipitated), $PbSO_4$ settled for 20 min. Solution filtered with suction. Ra assays made on filtrates.
(120)	Filtrate heated to boiling point, and a slurry containing 20 g. $BaCO_3$ added slowly. (Excess sulfate precipitated). Mixture boiled at constant volume for 30 min., cooled to room temperature, filtered using medium suction. Ra assays made on filtrate.

(Note: Times in parenthesis are estimated.)

i. Results of "Three-Step" Process:

Exp. No.	Slurry Vol ml.	Filtrate Vol ml.	% Ra in $PbSO_4$ filtrate	% Ra in $BaSO_4$ filtrate
D37*	150	74	0.033	0.045
D38	200	128	0.052	0.030
D39	150	69	0.097	0.017

* High Ra undoubtedly due to contamination of the aliquot sample taken.

j. Yale Lead Sulfate Cake Experiments: (Ref. li)

Raw Material:

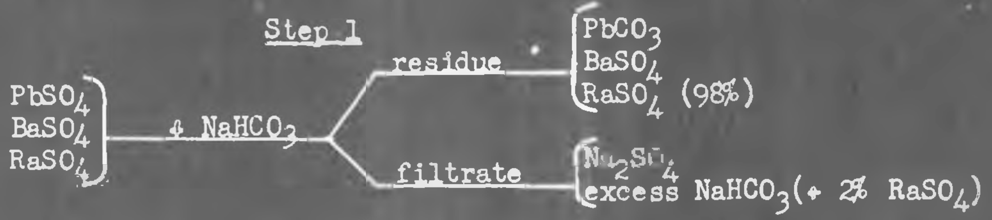
A typical lead cake resulting from the "three-step" process had the following analysis (from a 30 kg. digestion):

$PbSO_4$	96.9%
$BaSO_4$	1.3
SiO_2	0.3
R_2O_3	0.3
$CaSO_4$	<0.1
L.O.I.	0.6
$SrSO_4$	ca. 0.1
total	99.6

Ra content 16.6 x 10^{-7} g/g of cake
Ratio: Ba:Ra--4620:1

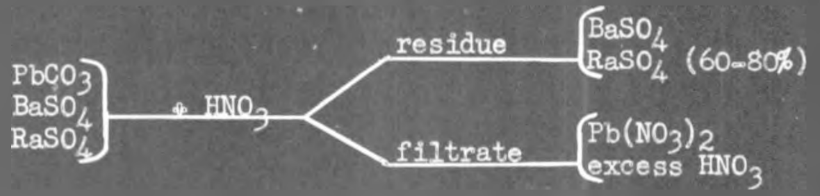
Sodium Bicarbonate Method:

Step 1



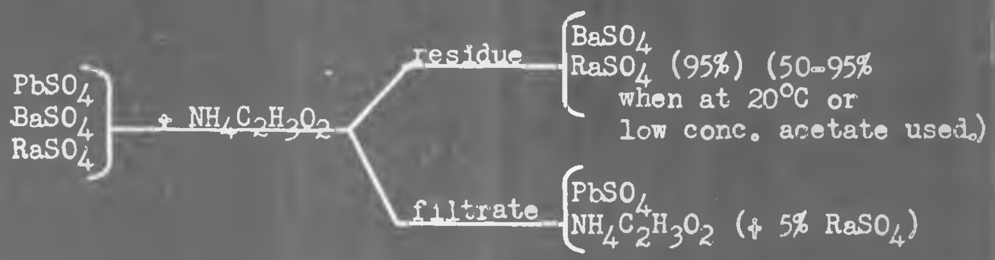
Cake treated with 10% solution of $NaHCO_3$ at 20°C for 3 hours. The amount of $NaHCO_3$ used is 3X theoretical.

Step 2



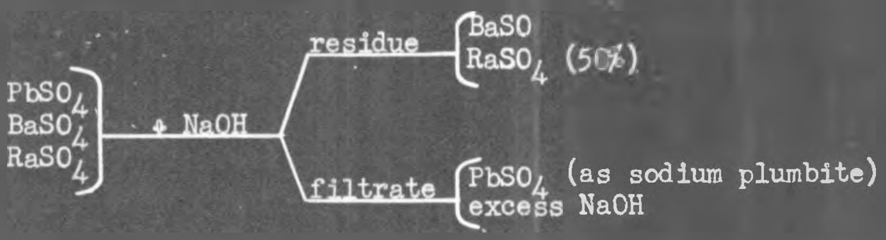
$PbCO_3$ cake decomposed with barely sufficient dilute HNO_3 at 20°C . A milky suspension results and requires overnight standing. This precipitate is primarily $BaSO_4$ with other minor constituents.

Ammonium Acetate Method:



Hot 50% ammonium acetate added to cake. (75 g. of acetate in 150 ml. of soln. is required to dissolve 10 g. of $PbSO_4$.) Mixture is stirred at 80-90°C for 1 hour, and filtered hot. Charcoal or filter pulp aids the filtration.

Sodium Hydroxide Method:



Cake treated with NaOH either at 20° or 85°C. 30 g. of NaOH is required per 10 g. of lead cake at 20°, and 20 g. of NaOH per 10 g. of cake at 85°C. These quantities of NaOH were dissolved in 500 ml. of water for use. Reaction is rapid at either temperature. The mixture is filtered, and the residue washed free of lead by dilute NaOH solution.

2. University of Rochester

a. Procedure for Coprecipitation of $RaSO_4$ with $PbSO_4$:

To a given volume of a nitric acid digestion solution from a high grade ore (of known Pb-Ra ratio), was added a known amount of sulfuric acid (or ammonium sulfate in some cases). The precipitation was done under various conditions, and the $PbSO_4$ that formed was filtered. The filtrate was analyzed for radium, and the percentage of radium precipitated was calculated. The acidity of the digestion solutions was altered for the experimental purposes by the addition of measured amounts of standard acid or base.

b. Results: (Quoted directly from 1g)

Influence of the SO_4/Pb ratio on the precipitation of Ra - The amounts of Ra unprecipitated from solutions having a variable sulfate-lead mol ratio were determined. In these experiments, other variables such as the Pb/Ra ratio, the temperature, the time of standing, and the acidity, were kept as nearly constant as possible. The results are contained below:

Number	$\frac{(SO_4)}{(Pb)}$	(H^+)	Percent Ra Precipitated
I-7	3	0.15	99.50
II-2	6.0	0.13	99.69
II-3	6.0	0.06	99.90
I-8	6.4	0.22	99.81
I-1	10	0.25	99.29
I-6	12	0.27	99.90
III-6	25	2.0	99.63
I-5	40	0.50	99.63

Pb/Ra = 1.56×10^6. Temperature, 25°C.
Stand 30 minutes before filtration.
Weight $PbSO_4$ precipitated, 275 mg.

Other data on the effect of the SO_4/Pb ratio are given below:

Number	$\frac{(SO_4)}{(Pb)}$	(H^+)	Percent Ra Precipitated
I-14	1.5	0.25	99.94
I-12	3.0	0.33	99.94
I-13	15.0	1.0	99.98

$Pb/Ra = 8 \times 10^6$. Temperature, 25°C.
Stand 30 minutes before filtration.
Weight $PbSO_4$ precipitated, 1610 mg.

Influence of temperature on the Ra precipitation - The results of experiments to determine the effect of temperature, keeping other variables constant, are given below:

Number	Temp., °C	Percent Ra Precipitated
I-1	25	99.89
I-2	100	98.13

$Pb/Ra = 1.56 \times 10^6$. $(H^+) = 0.25M$.
$(SO_4)/(Pb) = 10$. Stand 30 minutes
at stated temperatures before filtration.
Weight $PbSO_4$ precipitated, 275 mg.

Influence of standing time on the Ra precipitation - These data are given below:

Number	Standing Time Hours	Percent Ra Precipitated
I-1	0.25	99.89
I-1a	0.50	99.90
I-3	18	99.89

$Pb/Ra = 1.56 \times 10^6$. $(SO_4)/(Pb) = 10$.
$(H^+) = 0.25$ M. Weight $PbSO_4$ precipitated,
275 mg.

The influence of both time of standing and the temperature is shown below:

Number	Standing Time Hours	Temp., °C	Percent Ra Precipitated
I-3	18	25	99.89
I-4	22	40	99.90

Influence of the Pb/Ra ratio on the Ra precipitation - Data showing the effect of the Pb/Ra ratio on the completeness of recovery of Ra, other variables held constant, are given below:

Number	Pb/Ra	(H^+)	Percent Ra Precipitated
III-10	1.38×10^5	0.1	98.61
III-16	5×10^5	0.25	99.60
I-1	1.56×10^6	0.25	99.89
I-12	8×10^6	0.33	99.94
I-10	2×10^7	0.52	99.92

SO_4/Pb = 10, except in I-12 where value is 3. Temperature, 25°C. Stand 30 minutes before filtration.

3. Mallinckrodt Chemical Works (Also see Tables I and II)(Ref. 1k,t)

a. Procedure Details

Process "A": Ore and water were suspended and heated to about 200°F. Nitric acid was added over a 40 minute period and sulfuric acid was added to coprecipitate lead-radium sulfate. The sulfate ranged from 5 to 9 times the lead later found to have been present at the end of the nitric acid digestion.

Process "B": Ore was added to water in digester, and the slurry was heated to about 200°F. Nitric acid was added slowly, with good stirring. Barium nitrate solution, prepared by dissolving $BaCO_3$ in dilute HNO_3, was then added. The barium was calculated on the basis of 400,000 parts of barium per part of radium. Sulfuric acid was then added. Sulfate was computed to be stoichiometrically equal to the barium plus the lead content of the ore. (Since not all the lead dissolved during nitric acid digestion, the finished digestion solutions contained appreciable sulfate.)

Process "C": The residues from "A" and "B" were extremely gelatinous, and were difficult to handle on the 3'x1' rotary vacuum filters. Therefore, nitric acid was heated in the digester and the ore was added slowly to it. The remainder of the process was like process "B".

Process "D": Small amounts of uranium were undissolved in many of the "B" and "C" tests, and it was believed that sulfuric acid would prevent these losses. Therefore, after the ore was added to the heated nitric acid, sulfuric acid was added and the batch digested for about ½ hour. Barium nitrate was then added. For the first two tests the barium carbonate was predissolved in nitric acid, while in the remainder of the tests (and in process "E" and "F") the barium carbonate was added to the batch as a slurry in 10 gallons of water.

Process "E": In some tests there were indications that the addition of the barium was deleterious to both uranium and radium recovery. Therefore, the barium was omitted in "E", and the sulfuric acid concentration was varied. Nitric acid was placed in the digester, heated to about 200°F. Ore was added slowly with good agitation, and sulfuric acid was added. (Similar to process "D".)

Process "F": To provide the highest possible acid concentration for the ore, both nitric and sulfuric acids were added to the digester and heated before adding ore. After digestion, the batch was filtered without the addition of barium. The sulfate added was equivalent to slightly less than twice the PbO present in the ore.

b. Results of Research: (See Tables I and II.)

c. Mallinckrodt Production Process for Ore Digestion

The required amount of 45% nitric acid (about 0.175 gal. per pound of ore) is added to the digestion tank. Then the required amount of 66° Be' sulfuric acid is added (so that total sulfate is three times that required to precipitate all the lead), and the acids are agitated. The mixture is heated to 210°-215°F and held at this temperature throughout the ore addition.

A 1.5" vacuum is placed on the tank, and the Syntron feeder is started. Ground ore is added at such a rate that ½" of vacuum is maintained. Control of the addition rate is important to prevent excessive evolution of NO_2 and boil-over. [redacted] After all the ore is added, the batch is mixed for ½ hour at constant temperature. At this point, the batch is sampled for excess nitric acid (should be 0.3-0.5 lb. per gallon and is adjusted to this range with 45% acid or ore). The batch is ready for filtration. (Filter aid is added at this point if necessary.) The batch is kept at 200°-210°F during filtration.

TABLE I

√SUMMARY OF ORE ANALYSES/ [redacted]

Composition - %

Ore Designation	U	Ra(x10^{-8})	PbO	MoO_3	P_2O_5	SiO_2	H_2O
I	40.2	1.6	-	0.42	0.76	19.1	-
Max.var.	(2.6)	-	-	-	-	-	-
II	42.3	1.6	6.5	0.73	1.18	19.5	4.0
Max.var.	(1.4)	(0.2)	(1.6)	(0.46)	(0.37)	(0.1)	(0.3)
III	40.9	1.7	6.1	0.57	1.66	-	1.2
Max.var.	(5.7)	(0.0)	-	(0.05)	(1.00)	-	(0.8)
IV	47.1	1.8	6.0	0.55	0.69	20.6	2.7
Max.var.	(0.1)	-	(0.6)	-	-	-	(1.0)
V	47.1	1.8	6.1	0.58	0.70	-	-
Max.var.	(0.1)	(0.1)	(0.5)	(0.01)	(0.01)	-	-
VI	46.3	1.8	6.5	0.66	0.64	-	3.1
Max.var.	(1.4)	(0.1)	(0.1)	(0.01)	(0.14)	-	(1.3)
VII	66.6	2.3	6.8	0.60	0.11	10.2	0.9
Max.var.	(0.5)	-	(0.1)	(0.11)	(0.02)	-	(0.1)

ORE GRIND NOTES (See Process Data Summary)

a. Ball mill, 98-99% through 200 mesh.
b. Hammer mill, 90% through 200 mesh.
c. Dry ground, 65-75% through 50 mesh, 10-25% through 200 mesh.

DECLASSIFIED

TABLE II

SUMMARY OF PROCESS DATA [redacted]

Process	Exp. No.	Ore Used	Ore Grind Note	Calculated % HNO_3 Upon Digestion	U Added lb.	H_2SO_4, 66°Be' Added-lb.	$BaCO_3$ Added lb.	Concentration in Sludge After Digestion-g./l. U	Ra*	Eq.HNO_3	% Ra to Filtrate
A	I	I	a	30.4	137	54	0	316	0.5	65**	0.04
	L	I	a	29.4	127	46	0	246	2.2	-	0.22
	N	I	b	27.6	136	55	0	314	1.7	95**	0.14
	P	I	b	28.5	123	54	0	243	2.6	158	0.27
	R	I	a	21.8	107	48	0	227	1.0	-	0.11
										Average -	0.20
B	T	II	c	27.9	124	20.5	24.5	253	2.25	45**	0.24
	U	II	c	27.9	122	20.5	24.0	205	15.5	40**	2.00
	V	II	c	30.5	150	27.0	29.2	233	1.25	30**	0.14
	W	II	c	30.5	150	24.5	29.2	227	3.50	45**	0.41
	Y	II	c	30.3	145	25.0	29.2	286	12.5	-	1.16
	Z	II	c	30.3	153	25.0	29.0	232	6.5	-	0.74
										Average -	0.78
C	108	III	c	30.0	150	25.0	29.0	240	0.27	15	0.03
	109	III	c	30.0	156	25.0	29.0	250	8.0	48	0.77
	111	IV	c	30.5	150	25.0	29.0	249	13.0	30**	1.37
	112	IV	c	56.5	150	25.0	29.0	385	27.0	85	1.84
										Average -	1.00
D	113	V	c	56.5	150	25.0	29.0	410	1.1	-	0.07
	114	V	c	56.5	150	25.0	29.0	420	14.0	30**	0.87
	115	V	c	56.5	150	25.0	29.0	402	11.0	-	0.72
	116	V	c	56.5	150	25.0	29.0	420	33.0	45	2.04
										Average -	0.93
E	125	VI	c	56.5	151	25.0	0	325	16.5	45	1.30
	126	VI	c	56.5	152	25.0	0	342	7.0	45	0.53
	129	VI	c	34.3	149	25.0	0	393	4.1	120	0.27
	130	VI	c	34.3	150	25.0	0	355	4.3	95	0.31
	131	VI	c	34.3	150	12.0	0	312	8.5	80	0.70
	132	VI	c	34.3	150	18.0	0	299	3.9	45	0.24
										Average -	0.56
F	151	VII		39.6(41.8)***	200	18	0	460	4.4	105	0.28
	154	VII		39.6(41.8)***	200	18	0	461	6.0	105	0.38
										Average -	0.33

(continued on page 44)

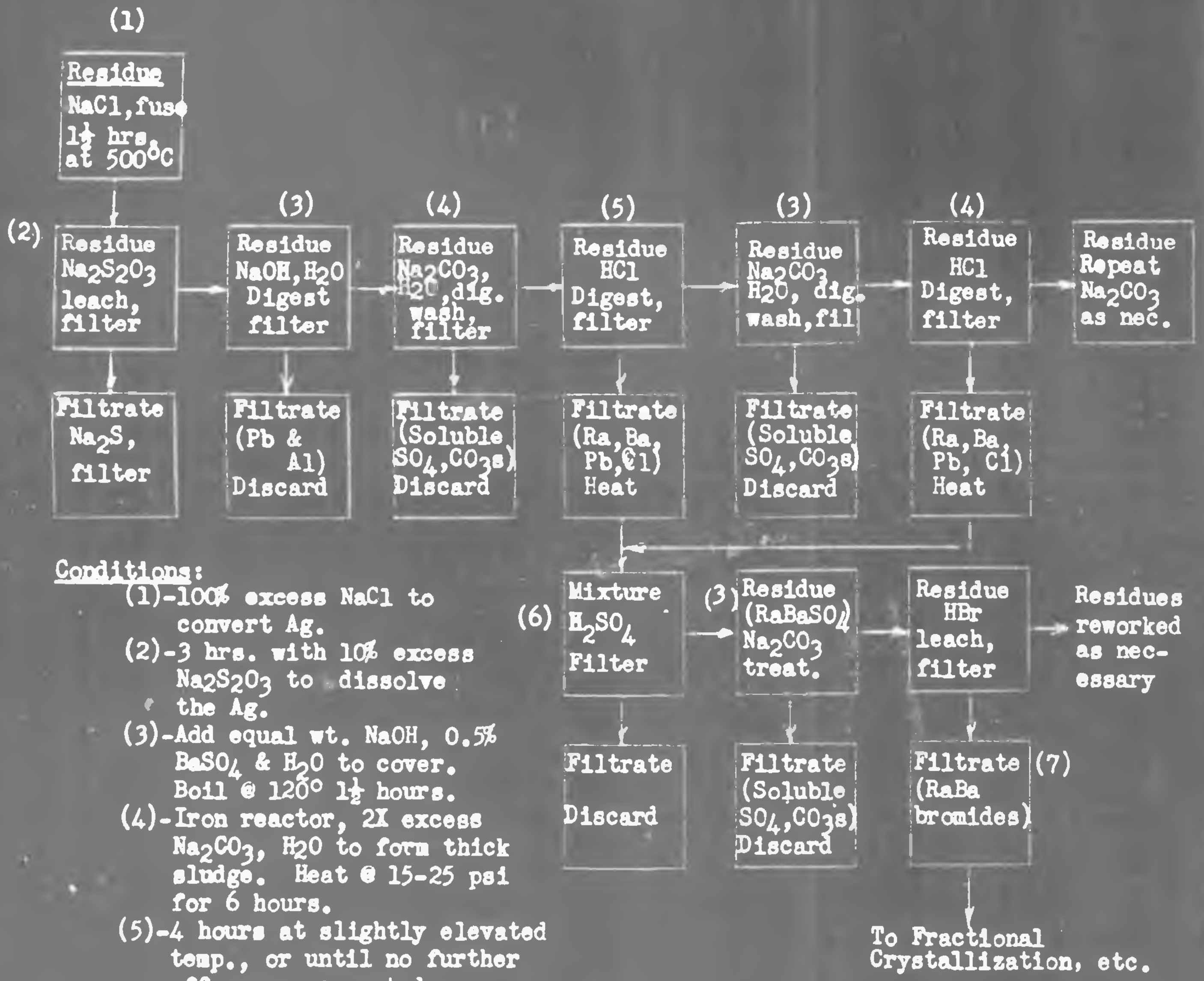
* Grams x 10^{-7}.

** Free HNO_3 concentrations at end of HNO_3 reaction before H_2SO_4 or $BaCO_3$ added. Not corrected for later additions.

*** Represents combined HNO_3 and H_2SO_4 expressed in terms of HNO_3.

Note: 135 gal. stainless steel digester. Digestion time 1-2 hours. HNO_3 was generally technical grade, 38°. Barium supplied as $BaCO_3$ (99.5% pure) and was converted to $Ba(NO_3)_2$ by predissolving in HNO_3. In Exp. 111 and afterward $BaCO_3$ was added directly to batch as a water slurry.

MONSANTO CHEMICAL COMPANY
MOUND LABORATORY
CURIE PROCEDURE



Conditions:

(1)-100% excess NaCl to convert Ag.

(2)-3 hrs. with 10% excess $Na_2S_2O_3$ to dissolve the Ag.

(3)-Add equal wt. NaOH, 0.5% $BaSO_4$ & H_2O to cover. Boil @ 120° 1½ hours.

(4)-Iron reactor, 2X excess Na_2CO_3, H_2O to form thick sludge. Heat @ 15-25 psi for 6 hours.

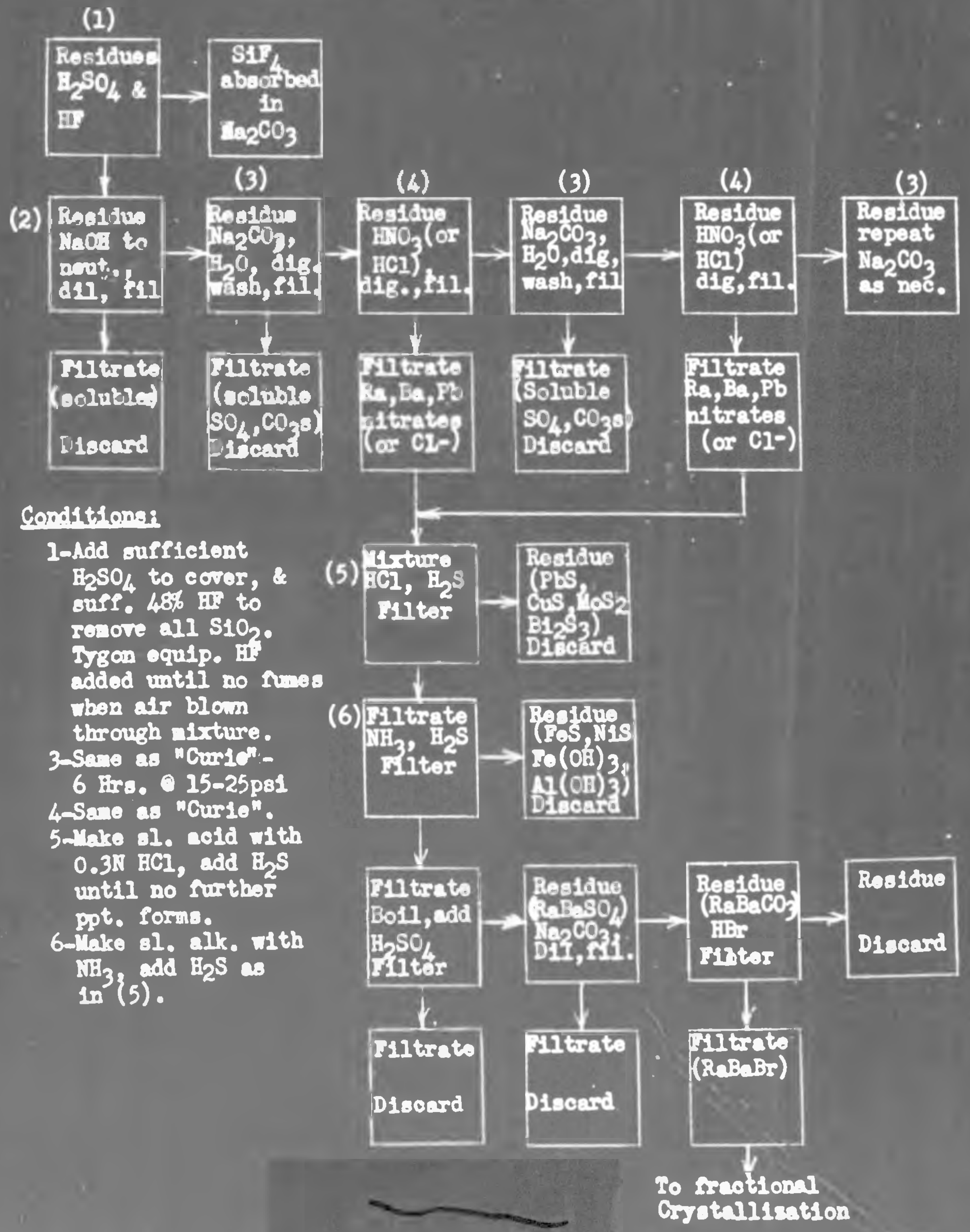
(5)-4 hours at slightly elevated temp., or until no further effervescence noted.

(6)-Add H_2SO_4 to boiling solution until no more precipitate formed.

(7)-BaS & BaOH may be added to remove last traces of Pb.

NOTE: Filtration of slurry from first (3) carbonate treatment tried with Buchners (with coarse and fine paper) using vacuum, pressure, vacuum & pressure, fritted glass, but none worked. Centrifuging slow and tedious. Centrifugate removed by decantation. Residue washed with 10% Na OH and recentrifuged.

MONSANTO CHEMICAL COMPANY
MOUND LABORATORY
MODIFIED CURIE PROCEDURE



Conditions:

1-Add sufficient H_2SO_4 to cover, & suff. 48% HF to remove all SiO_2. Tygon equip. HF added until no fumes when air blown through mixture.

3-Same as "Curie"- 6 Hrs. @ 15-25psi

4-Same as "Curie".

5-Make sl. acid with 0.3N HCl, add H_2S until no further ppt. forms.

6-Make sl. alk. with NH_3, add H_2S as in (5).

DECLASSIFIED

Date of Manuscript: October 31, 1947

SEPARATION OF RADIUM FROM BARIUM BY THE USE OF AN ION-EXCHANGE COLUMN PROCEDURE

By Edward R. Tompkins

In current radium production processes, the radium and barium are separated by fractional crystallization, the method originally developed by the Curies. This is a very tedious process, which requires many recrystallizations and extensive recycling of the various fractions to obtain a clean separation without excessive losses. To carry out this procedure without endangering the safety of the operating personnel requires considerable remote control equipment, and because of the large number of operations, contributes appreciably to the present cost of radium.

In the course of extensive investigations of ion-exchange separation methods for the preparation of pure fission products,[1] it was noted that microgram quantities of strontium and barium (two of the fission elements) could be readily separated by this method. The separation, which depends chiefly upon the differences in the dissociation constants of the barium and strontium citrate complexes, was made by first adsorbing the mixture at the top of a bed of synthetic ion-exchange resin, Amberlite IR-1, 100 cm in length, and subsequently eluting the elements preferentially from this column by the use of complexing agents at carefully adjusted values of pH. By exercising considerable care, it was possible to effect nearly complete separation of the barium and strontium in these low concentrations, although the separation was much poorer when milligram quantities of these elements were present. The apparatus was simple and was thus easily adaptable to remote control procedures.

Recently, samples of several new organic exchangers have been obtained.[2] One of these, Dowex 50, has a much higher combining capacity than any exchanger tested here previously. Because of this it is much more applicable to the separation of ponderable quantities of materials. Extensive studies of this resin for rare earth separations[3,4,5] had shown the importance of using small particle sizes and/or elevated temperature to obtain optimum results. A special sample of colloidal agglomerates of Dowex 50 had proved especially effective for rare earth separations, a column of this resin 10 cm in length giving a better separation than had been obtained with a 100 cm column of Amberlite resin under similar conditions.[4]

From these results and the earlier observations regarding the behavior of strontium and barium when eluted from Amberlite resin columns, it appeared that a good separation of barium from radium should be possible by the use of a short column of the new resin. Because of the much greater affinity of Dowex 50 resin for cations (as compared to IR-1), it was necessary to determine the correct conditions for the elution of the alkaline earths from this resin. Whereas the separation with IR-1 had been made by eluting strontium and barium with 0.23M citrate at pH 4.75, preliminary experiments with strontium showed that it was necessary to use 0.5M citrate at pH 7.5 to 8.0 to remove it from Dowex 50 at a convenient rate. It was also shown that barium and strontium in trace concentrations could be separated by elution from a column of colloidal agglomerates of Dowex 50, 1 cm^2 x 15 cm.

This column of colloidal agglomerates was next employed to test the separation of barium from radium. The starting solution containing 20 μc (20 μg) of radium, 20 mg of barium with Ba^{140} tracer (and La^{140} daughter), and 20 mg of strontium with $Sr^{89,90}$ tracer was first slowly passed through the column, causing the solute mixture to be adsorbed at the top. Ammonium citrate solution, 0.5M, was then passed through the column at a rate of 0.3 ml per minute, the effluent being monitored by means of a special apparatus consisting of thin-windowed flow cell facing a mica-windowed Geiger-Mueller counter tube which was attached to a counting rate meter and recorder. By means of this apparatus it was possible to obtain a continuous record of the concentration of the beta and gamma emitters in the effluent from the column. A reproduction of this recorded curve is shown by the solid, curved line in Figure 1.

Fractions of the effluent solution were collected at the stages indicated on this curve (I to XVIII), and aliquots were counted for alpha, beta, and gamma activity. Aluminum absorption and decay curves of these radioactivities were taken, as a method of determining the composition of each fraction. From these results the approximate composition of the various fractions and the percentage of each element in each of the various fractions were calculated. Table 1 summarizes this data.

Table 1. Composition of eluate fractions from separations column.

	Per cent of total				Percentage composition of fractions				
Fraction	La	Sr	Ba	Ra	La	Sr	Ba	Ra	Ra decay products
I	16.7	2.0	-		88	12	-	-	
II	75.0	4.4	-		97	3	-	-	
III	1.1	6.3	-		6	94	-	-	
IV	0.0	79.5	-		-	100	-	-	
V	1.0	7.7	-		14	86	-	-	
VI	0.4	0.1	-		82	18	-	-	
VII	5.8	-	82.5		27	-	73	-	
VIII	-	-	15.9		-	-	86	-	14
IX	-	-	1.6		-	-	50	-	50
X	-	-	-	-	-	-	-	-	100
XI	-	-	-	-	-	-	-	-	100
XII	-	-	-	-	-	-	-	-	100
XIII	-	-	-	9.4				100	
XIV	-	-	-	24.8				100	
XV	-	-	-	40.6				100	
XVI	-	-	-	22.5				100	
XVII	-	-	-	2.6				100	
XVIII	-	-	-	0.1				100	

In making the column run, the flow of elutrient solution was stopped overnight (17 hours) after fraction VI had been collected. This allowed the La^{140} daughter of the Ba^{140} (which was still adsorbed on the column) to grow back to about 20% saturation, thus affecting the shape of the recorded elution curve for the barium. Because the energy of the radiation from the daughter element is greater than that from the barium, the effect was accentuated in the recorded curve. The estimated elution curve for barium is shown by the broken curved line. The beta and gamma emitters in fractions X to XII

[redacted]

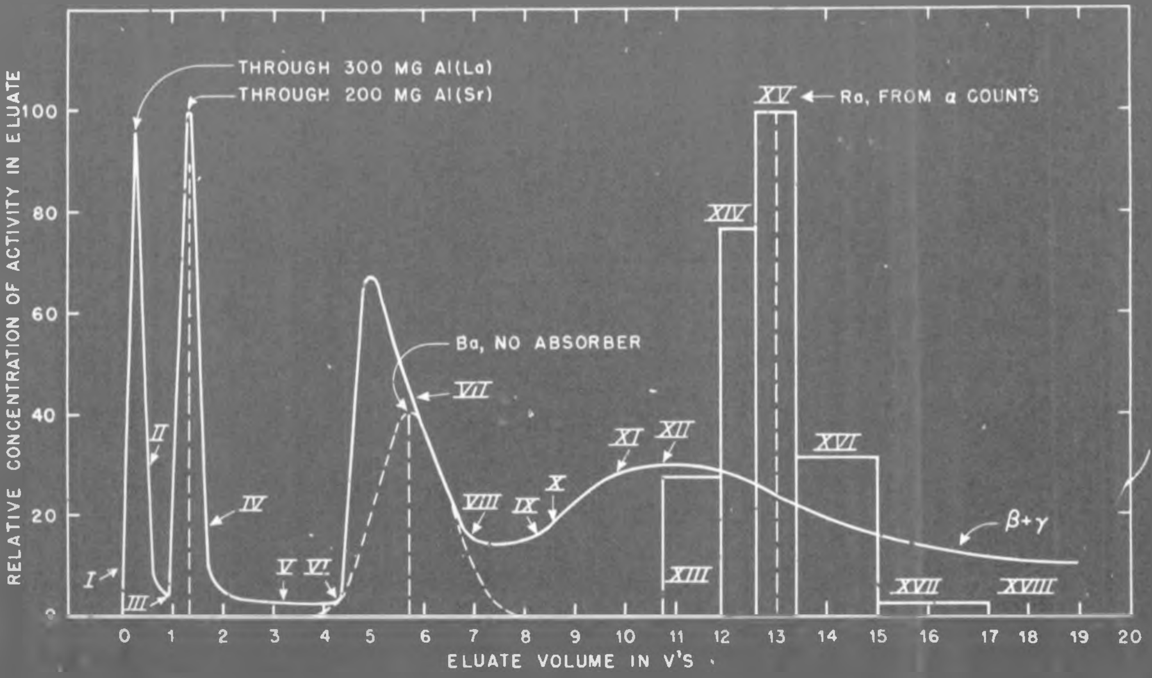


Figure 1. Separartion of Sr, Ba, and Ra.

inclusive decayed with a half-life of several hours (radium decay products), indicating that no detectable barium was present in these fractions.

From Table 1 it can be seen that the separation of strontium and barium and of barium and radium was nearly complete. (The failure of the recorded curve to fall to zero in the zone between strontium and barium is due to the continuous elution of La^{140} which was formed by the decay of Ba^{140} on the column.) Radium was detected by its alpha activity. Sample XII showed the first alpha activity, but it decayed rapidly to a very low count, showing that it was chiefly radium decay products. The radium elution curve is shown graphically in Figure 1, where radium concentration in the eluate (in arbitrary units) is plotted versus the eluate volume. It will be noted that essentially all the radium was contained in samples XIII to XVII inclusive.

The results of this investigation indicate that the separation of radium from barium on a commercial basis could be much more easily effected by this column method than by the current procedure based on fractional crystallization. The method is simple to operate and thus may be easily adapted to remote control. The use of this separation method for the quantitative analysis of radium has not been investigated, but it is probably applicable.

REFERENCES

1. Tompkins, E. R., J. X Khym, and W. E. Cohn, J. Am. Chem. Soc. 69:2769 (1947).
2. Through the courtesy of W. C. Baumann, The Dow Chemical Company, Midland, Michigan.
3. Harris, D. H. and E. R. Tompkins, J. Am. Chem. Soc. 69:2792 (1947).
4. Tompkins, E. R. and S. W. Mayer, J. Am. Chem. Soc. 69:2859,2866 (1947).
5. Ketelle, B. H. and G. E. Boyd, J. Am. Chem. Soc. 69:2800 (1947).

[redacted]

6. Linde Air Products Company (Ref. 1s,t)

a. Laboratory Research (Ref. 1t)

In one series of tests, 100 g. samples of pitchblende ore (about 10% U_3O_8) were digested with about 100 g. of 96% H_2SO_4 in an acid concentration of 50%, with the addition of 8 to 21 g. of HNO_3 or of 7 to 12 g. of $NaClO_3$ as the oxidizing agent, and with 0 to 2 g. of $BaCl_2$. After filtration, both the residue and the filtrate were analyzed for radium; the analyses of the filtrates were more consistent, probably due to difficulties in sampling the residues. The average analysis of twelve filtrates indicated that considerably less than 0.01% of the total radium was in solution; the average analysis of the corresponding residues accounted for more than the original weight of radium.

A second series of laboratory experiments was performed more nearly according to the proposed plant procedure by digesting the 100 g. samples in 10% sulfuric acid with MnO_2 or HNO_3 as the oxidizing agent and with 1 g. of $BaCl_2$. After digestion, the mixture was treated with 114 to 200 g. of Na_2CO_3 and filtered. In eight experiments, the average analysis of the alkaline filtrate showed the presence of about 0.10% of the total radium, while analysis of the residues again gave more erratic results, with an average somewhat in excess of 100% of the radium in the original ore.

b. Pilot Plant Research (Ref. 1s)

Procedure: Same as Plant Production Procedure below

[redacted]

Results:

DIGEST SUMMARY

	Dig. A-1	Dig. A-2	Dig. A-3	Dig. A-4	Dig. A-5	Dig. A-6	Dig. A-7
Lb. Ore (wet)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Lb. Ore (dry)	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
% U_3O_8	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Lb. U_3O_8	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Lb. H_2SO_4 (per 100 lb. wet ore)	7.76	6.92	11.42	7.85	9.39	7.45	7.25
Lb. MnO_2 (per 100 lb. wet ore)	4.0	4.0	4.0	4.0	4.0	4.0	2.00
Lb. $BaCl_2$ (per 100 lb. wet ore)	1.0	1.0	1.0	1.0	1.0	1.0	0.10
Final Acid Digest pH	2.94	3.02	2.06	2.00	2.03	1.98	2.0
Soda Ash (per 100 lb. wet ore)	27.4	35.3	89.1	33.8	33.8	34.2	35.4
Final Alkaline Digest pH	9.2	9.23	9.9	9.84	9.38	9.45	9.12
Type of Neutralization	Reverse	Reverse	Direct	Direct	Reverse	Direct	Direct

Remarks: pH after alkaline digest of A-7 was 9.12. 9.53 lb. of acid per 100 lb. wet ore were used after alkaline digest to bring pH to 8.22 for 2nd digest period. 1 lb. of ferric sulfate per 100 lb. wet ore was added to digest for 2nd digest period.

RADIUM DISTRIBUTION

Sample	Radium Gm./gm.	Radium Gm./100 Ml.	Gal. Filtration Liquors	Heads Tons	Tails Tons	U_3O_8 Tons	Total Radium Mg.
Composite Heads from Digests 1-6	2.21×10^{-8}			[redacted]			373.5
Composite Tails from Digests 1-6	2.21×10^{-8}				[redacted]		332.6
U_3O_8 from 1st Digest	7.18×10^{-11}					0.243	0.0158
Heads from 7th Digest	2.24×10^{-8}			2.95			59.9
Tails from 7th Digest	2.19×10^{-8}				2.81		56.0
Filtration Liquors							
1st Digest		4.16×10^{-11}	4260				0.00674
2nd Digest		4.93×10^{-11}	5130				0.00958
3rd Digest		7.02×10^{-11}	7150				0.0190
4th Digest		2.51×10^{-11}	7180				0.00684
5th Digest		3.18×10^{-11}	7080				0.00854
6th Digest		5.84×10^{-11}	5500				0.0122
7th Digest		5.72×10^{-11}	6500				0.0141
Decant Liquor from Molybdenum Removal							
1st Digest		8.8×10^{-12}	4450				0.00148

d. Linde Research Production Procedures

After wet ball-milling, the ground ore (containing about 6 to 10% U_3O_8) as a slurry was pumped to wooden digestion tanks. [redacted] 66° Be' sulfuric acid was added to a pH of 1.1 to 1.3 and the resulting slurry was heated to 90°C. MnO_2 was added to oxidize the tetravalent uranium. The pH of the mixture was again adjusted to 1.1 to 1.3. During the acid digestion of three hours, a hot solution of $BaCl_2$ in water was slowly added to the tank.

After the digestion was complete, the batch was cooled to 60°C or less. Dry soda ash was added to a pH of 9.5 and the basic mixture was heated to 90°C and digested for 1 hour. The slurry of precipitate and uranium solution was then filtered, the residue was sent to storage, and the filtrate was sent to the uranium purification plant. (Well over 97% of the radium in the ore was sent to storage in the sludge during the year and a half of production using low grade ores.)

7. Properties of Versene

Versene (ethylene diamine tetra acetic acid) is a strong complexing (chelating) agent. The complexes are so strong that such compounds as $BaSO_4$ and $PbSO_4$ are easily dissolved. As the system is very dependent on pH, it is proposed to adjust pH of the solution to the point where Ba and Pb sulfates will not precipitate, but where the Ba will be absorbed on the ion exchange resin and thus separated from the sulfate. (Ref. 1d)

Equilibria in $BaPbSO_4$ system was considered by Schwarzenbach in <u>Heh. Chemica Acta 30.</u> 1798 (1947) and 21, 1029, (1948) and from this work the amount of free Ba present can be calculated for any pH and Versene concentration. At pH 6.5-7, the per cent Ba complexed is low while Sr and especially Pb are still in complexed form. If equilibrium constants for Pb were known, it would be possible to calculate the minimum amount of Versene needed to dissolve Ba and $PbSO_4$ at pH 6.5 from the fact that the amount of free Ba should not exceed the K_{sp} of $BaSO_4$. Empirical experiments show that $7.1\text{-}7.9 \times 10^{-3}$ moles of Versene are the minimum necessary to dissolve 1 g. of Pb and 10 mg. Ba as sulfates, and 10 mg. each of Fe, Cu, Ni at a pH of 6.5 in 50-60 ml. of solution. (Ref. 1e)

General Versene Procedure: (Ref. 1f)

a. Pb-$BaSO_4$ ppt. dissolved in 0.1 M Versene at pH 6.3 and absorbed on a Dowex 50 bed. Ba and 50% of Sr are absorbed, all other ions passing through as anion complexes (Pb, RE, Fe).

b. Ba eluted with 0.23 M Versene at pH 11.

c. Ba solution adjusted to pH 4 and absorbed on 2nd Dowex 50 bed.

d. Sr eluted with 0.1 M Na nitrate at pH 9.

e. Sodium eluted with 0.5 M HCl.

f. Ba product eluted with 6 M HNO

E. Analytical Procedures (Ref. 1t; 3e,f,g)

1. Yale University (Ref. 1t; 3e,f,g)

a. Perchlorate Procedure:

This procedure is applicable to samples containing but little sulfate. It fills a need for a rapid procedure of sufficient simplicity so that a large number of samples can be handled simultaneously.

A sample of the material to be assayed containing no more than about 5×10^{-8} g. of radium is weighed into a platinum crucible. If an untreated ore is under examination, it is decomposed in the crucible with a little HNO_3 or HCl. 1-2 ml. of pure $HClO_4$ and 10 ml. of 50% HF are added, and the mixture is carried to dense fumes of $HClO_4$ on the hot plate. After cooling, the residue is dissolved in a few ml. of water. At this stage, there often remains a small precipitate which presumably consists largely of $PbSO_4$. A considerable quantity of ashless paper pulp is now stirred into the solution, which is passed through a well washed filter into the container designed for the final sample. After washing the paper free of $HClO_4$, the paper is transferred to the original platinum crucible. The crucible is covered and the paper decomposed by strong heating. This procedure is designed to give reducing conditions in the crucible to decompose any sulfate. The cover is then removed and the ignition concluded under oxidizing conditions. At this stage, a small reddish-yellow residue, presumably Pb oxides, usually remains. This residue is now fused with pure Na_2CO_3 until a clear fusion is obtained. The melt is covered with water and $HClO_4$ is added cautiously under the lid of the crucible. When all action has ceased, HF is added, and the solution is carried to fumes on the hot plate. If, after the addition of water, any residue remains, the procedure is repeated, beginning with the addition of paper pulp. Usually, however, a perfectly clear solution is obtained which may be added directly to the main bulk of the sample. The final sample is examined under a bright transverse beam of light. Any suspended matter other than a very few particles of dust or paper lint causes the rejection of the sample. Radium is then determined by usual emanation procedures.

This method is good to about 20%, but since the radium in the filtrates is generally about 1% of the original radium, the accuracy based upon the original radium is about 0.2%. Where the radium to be determined is considerably greater than 1% of the input radium, the error may approach 20% of the input radium.

b. The Sulfate Method:

A sample of appropriate size, solution or solid, is repeatedly taken to fumes with sulfuric and hydrofluoric acids. The mixture is diluted with water, and barium chloride solution is added so that the Ba-Ra ratio will be about 1,000,000 to 1. The precipitate is digested at the boiling temperature, and filtered. After ignition, the precipitate is dissolved in excess concentrated sulfuric acid and again fumed with hydrofluoric acid. The acid solution of sulfates is poured into water, and the resulting precipitate is filtered and ignited. It is then fused with ten times its weight of Na_2CO_3. The nearly clear fusion is cooled quickly and leached with hot water. The residue is dissolved in nitric acid. This acid solution is ready for de-emanation.

This procedure is tedious and requires much platinum. Samples containing Pb seriously attack the platinum during fusion. The accuracy of the procedure is only fair, but when small residual amounts of radium are to be determined, the method is considered to be of adequate accuracy.

2. Mound Laboratory (Ref. 1a)

a. Rapid Method: Relatively pure radium-barium samples are used for this procedure. The radon is removed from the sample by drawing air through the solution. After clearing, the sample is aged for a specified time so that the radon and daughter products can build up again. Then, an aliquot is rapidly pipetted on a slide, dried, and counted as quickly as possible. The quantity of radium present in the original sample can then be calculated using previously determined calibration data.

b. Accurate Method: (See standard emanation method.)

3. Kellex Corporation (Ref. 1b)

Rapid Method (adapted from Argonne National Laboratory procedure): After removing lead and silica, radium and barium sulfates are converted to carbonates and dissolved in hydrochloric acid. An aliquot is treated with barium chloride solution. Barium and radium chlorides are then separated from all other alpha emitters by precipitation upon treatment with seven volumes of ice cold hydrochloric acid-ether reagent (ratio of 6 to 1). After washing, the chlorides are dissolved in water and transferred to a counting plate where they are again converted to sulfates. The alpha activity is determined by a standard parallel plate alpha counter. This method has an accuracy of about ± 10% which is sufficient for exploratory purposes.

4. Standard Emanation Procedure (National Bureau of Standards) (Ref. 3d)

The radium in ores or residues must first be dissolved to permit later measurement of the radon. Pitchblende ore samples are prepared as follows: A 1 gram sample of ore is weighed into a beaker, wet with water, and 50 ml. of HNO_3 (1 + 1) is added. The

[redacted]

mixture is covered with a watch glass, and heated just below boiling for at least one hour. The solution is diluted to 75 ml. with water and filtered through a Whatman No. 42 filter paper into a 1 liter volumetric flask. The insoluble residue is washed thoroughly with warm water. The filter paper and residue are ignited in a 25 ml. platinum crucible. A little water and 20 ml. of HF are added to the residue, and the solution is evaporated to dryness on a hot plate. The residue is fused for one hour with 8 grams of Na_2CO_3. The melt is cooled, and dissolved in dilute HNO_3, adding the solution to the filtrate in the volumetric flask.

Residue samples (i.e. K-65) are prepared as follows: A 0.2000 gram portion of the ground sample is placed in a 100 ml. platinum dish, moistened with water, and 20 ml. of $HNO_3(1 + 1)$, 10 ml. of $HClO_4$ (70%), and 20 ml. of HF are added. The dish and contents are heated on a hot plate to dryness. 20 grams of ammonium acetate and 5 ml. of water are added and mixed with the dry residue. The dish is covered, and digested on a steam bath for 15 minutes. Then, 15 ml. of HNO_3 and 10 ml. of water are added. After standing for 10-15 minutes, the mixture is stirred and filtered through a No. 42 filter paper into a 1 liter volumetric flask. The paper and insoluble residue are washed thoroughly with water. The filter paper and contents are transferred to a platinum crucible and ignited until all the paper is ashed. The residue is fused with Na_2CO_3 for one-half to one hour. After cooling, the crucible and contents are placed in a 600 ml. beaker, 400 ml. of water and then 60 ml. of HNO_3 are added. After the sample is completely dissolved, it is transferred to the 1 liter flask containing the first filtrate. After making up to volume and measuring, a 50 ml. aliquot is used for radium analysis.

Radon is then determined on either solution as follows: 100-200 ml. of solution are used which contain about 10^{-9} grams of radium (although radium can vary from 10^{-8} to 10^{-13} grams). The solution, put in a flask fitted with a reflex condenser, is de-emanated by boiling for 17-18 minutes at about 7½ p.s.i.a. while N_2 is bubbled through it. The flask is then sealed off by stopcocks at atmospheric pressure and the radon is allowed to collect for a convenient time, usually 24 hours. The amount of radium collected (in curies) is equal to $M_{Ra}(1-e^{-\lambda t})$, where M_{Ra} is the grams of Ra in solution, t the collection time in hours, and $\lambda = 0.00755/hr.$ The practical limit to collection time is about 30 days.

The radon is transferred to the evacuated ion chamber by reboiling and allowing nitrogen to sweep the radon into the chamber. (The nitrogen is purified by passing it through hot reduced copper to remove O_2, through Drierite and P_2O_5 to remove water, and through Ascarite to remove CO_2). The radon is allowed to come to equilibrium for at least 3 hours, and the count is usually made for

12 hours during the night.

The average count per hour above background is divided by $K(1-e^{-\lambda t})e^{-\lambda t}$, where K is the counts per hour determined by running a 10^{-9} gram radium standard solution, T is the decay time (from transfer time until counting is started), and other symbols are as defined above. If the calibration count is made for the same period as the sample, no additional correction is necessary.

F. Bibliography

1. Research References

a. Personal Communication from Babcock, A. B. to F. M. Belmore, "Visit to Mound Laboratories, Miamisburg, Ohio", March 16, 1950.

b. Bain, W. A. (Kellex Corporation), "March Progress Report", KLX-1201, April 7, 1950.

c. Personal Communication from Belmore, F. M. to W. E. Kelley, "Recovery of Radium at the Mallinckrodt Chemical Works", March 3, 1950, (summary of other work and recommendations).

d. Eister, W. K. (Technical Division, Oak Ridge National Laboratory), "Progress Report for Month Ending September 30, 1949", ORNL-519.

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

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

g. Flagg, J. F. (Rochester), "The Co-precipitation of $MySO_4$ by $PbSO_4$", M1586, November 1944.

h. Harned, H. S. (Yale University), "Final Research Report, Contract W-7412 eng-22", A-3772.

i. King, E. J., Thomas, H. C., Tomcufcik, A. S., (Yale University), "Progress Report on 'Lead Sulfate Cake' Experiments", received June 29, 1945, (Case No. 6886, MFC-11172).

j. Monsanto Chemical Company, (Quarterly Report, Mound Laboratory, for October, November, December, 1949), MLM-405-3.

k. Ritchie, C. F., "Separation of Radium from Uranium by Co-precipitation from Nitric Acid Solutions of Pitchblende Ore", MCW-15, April 1, 1946.

l. Personal Communication from Suesser, C. to W. E. Kelley, "Recovery of Radium from Pitchblende Ore", January 17, 1949, (summary of CNL and Yale work), (in Materials-5, Radium).

m. Thomas, H. C. and Miller, J. L. (Yale University), "Distribution of My in Nitric Acid Digestion of Pitchblende; Qualitative Notes on Filterability of Gangues".

n. Thomas, H. C. and Tomcufcik, A. S. (Yale University), "Distribution of My in Nitric Acid Digestions of Pitchblende", received October 17, 1944, (attached to "Progress Report for September 1944", by H. S. Harned (Case No. 5441).

o. Thomas, H. C. (Yale University), "Distribution of Radium in Nitric Acid Digestions of Pitchblende", (Summary Report), received June 28, 1946, (Case No. 3208).

p. Tomcufcik, A. S. (Yale University), "Progress Report of Modification of the Yale Process; Discussion of My Recoveries and Filtration Rates", August 28, 1945, (MFC-11224).

q. Tompkins, E. R., et al (Clinton National Laboratory), "Ion Exchange as a Separations Method", MonC-471, May 1947.

r. Ibid, "Separation of Radium and Barium by Use of an Ion Exchange Column Procedure", AECD-1998, October 31, 1947.

s. Weisendanger, R. (Linde Air Products Company), "Extraction of Uranium from Low Grade African Ore - Pilot Plant Operations", May 26, 1944.

t. Vance, J. E., "Uranium Technology", NNES Vol. 112A Chapter VII, (summary of other work).

2. Process References

a. Anonymous, "Engineering of Radium Production", Canadian Chem. and Process Ind., 125-128, 131, April 1938.

b. Personal Communication from Burman, L. C. to F. M. Belmore, "Radium Processing at Port Hope", January 11, 1949, (in Materials-5, Ra Resources).

c. Doerner, H. A., "Metallurgy of Radium and Uranium", Chapter XXIII in "Handbook of Non-Ferrous Metallurgy", by D. M. Liddell, McGraw-Hill, 1945.

d. Doerner, H. A., "Process for Extracting Radium from Carnotite", U.S.B.M. Report of Investigations No. 3057, December 1930.

e. Handley, R. W., "Procedure for Extraction and Recovery of Uranium and Radium from Ores of Same", Union Mines Development Corporation, July 15, 1946.

f. Mactaggart, E. F., "Radium Production", Chem. & Met. Eng., 178-181, July 1943.

g. Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. IV.

h. Linde Air Products Company, Ceramics Plant, "Construction, Process and Operation Report", M-333(II), October 1, 1946.

i. Miscellaneous correspondence, "Materials 2 (Sludges)".

j. Pochon, M., "Radium Recovery from Ores", Transactions, A. I.Ch.E; 33, 189-196, (1937).

k. Pochon, M., "Radium Extraction from Pitchblende at the Port Hope Refinery", from The Miner, II, No. 10, 34-38, (October 1938), Vancouver.

l. Prost, E., "Le Radium Sources de Production - Traitement des Minerais", Revue Universelle des Mines, Liege, Series 8, Vol. 14, No. 10, 741-751, (1938).

m. Sargent, E. C. and Reichard, H. F., "Radium Cake Storage", April 22, 1949. (NYO report).

n. Singer, et al (B.I.O.S.), "The Cerium Industry in German Territory Including Reports on Radium and Mesothorium", NP-39, September 1945.

o. Tyler, P. M., "Radium", U.S.B.M. Information Circ. 6312, August 1930.

p. Union Miniere du Haut Katanga, "Radium", (undated).

3. Analytical References*

a. Ames, D. P., et al (U. of Chicago Met. Lab.), "Rapid Radiometric Assay for Radium, and Application to Uranium Ore Process Solutions", AECD-2696, (declassified September 1, 1949).

b. Frueman, P., et al, "An Emanation Method for Radium Analysis", AECD-2620, May 3, 1946.

c. Lofthouse, E. (Imp. Chem. Ind. Ltd.), "Determination of Radium in Ore Concentrate Sludges", BR-716, June 21, 1946.

(*Only d to g read)

d. Neidrach, L. W., Mitchell, A. M., and Rodden, C. J., "Analytical Chemistry of the Manhattan Project", Chap. XXVI, AECD-2159, July 23, 1948, (or secret report MFC-5320, received March 29, 1948).

e. Thomas, H. C. (Yale University), "Report (1) on Radium Analysis", (attached to Progress Report for April 1944, by H. S. Harned), (MFC-15792).

f. Ibid, "Radium Analysis (Progress Report)", (attached to Progress Report for May 1944, by H. S. Harned), (MFC-13375).

g. Thomas, H. C. Tomcufcik (Yale University), "Revised Procedure for My Assay on Residue from Nitric Acid Digestion of Pitchblende", received June 12, 1945, (MFC-15844).

h. References 1a, 1b, 1h, 1t, 2d, 2g, 2p.

4. Availability and Procurement References (All Personal Communications except as noted).

a. Belmore, F. M. to W. E. Kelley, "Availability of Radium", February 21, 1950.

b. Chadwell, H. M. to W. J. Williams, "Radium Content of Sludges Stored in the U. S.", December 8, 1949.

c. Duffey, Dick, "Summary, from the Standpoint of Control, of the Radium Situation", (AEC Report), December 21, 1948.

d. Fisk, J. B. to W. E. Kelley, "Procurement of Radium", June 4, 1948, (in Materials-5, Ra Resources).

e. Kelley, W. E. to W. J. Williams, "Procurement of Radium", May 18, 1948, (in Materials-5, Ra Resources).

f. Manning, W. M. to J. B. Fisk, "Recommended Survey of Radium Resources", November 28, 1947.

g. Merritt, P. L. to Files, "Procurement of Radium", May 18, 1948, (in Materials-5, Ra Resources).

h. Merritt, P. L. to J. K. Gustafson, "Procurement of Radium", December 8, 1948, (in Materials-5, Ra Resources).

i. Ibid, August 24, 1949.

j. Merritt, P. L. to J. K. Gustafson, "Radium", January 17, 1949, (in Materials-5, Radium).

~~CONFIDENTIAL~~ ~~CONFIDENTIAL~~

k. Merritt, P. L. to J. B. Fisk, "Survey of Radium Resources", April 13, 1949, (in Materials-5, Ra Resources).

l. Merritt, P. L. to Files, "Supply of Radium", March 17, 1950.

[redacted]

~~CONFIDENTIAL~~

DECLASSIFIED